Metals emitted by the young submarine volcano Tagoro (El Hierro, Canary Islands): quantification in seawater and plankton and their potential impact

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Abstract

The concentrations of twenty metal elements in seawater and in plankton around the recently erupted submarine volcano Tagoro just South of the island El Hierro (Canary Islands, Spain) were investigated in order to assess their potential hazard to the marine environment. Samples of the seawater and the plankton were collected from 2013 to 2016 during the Vulcano and Vulcana monitoring cruises, using a rosette with Niskin bottles and a WP2 net (200 μm mesh size). Significantly higher concentrations of many metals were found in both the seawater and the plankton around the volcano compared to reference stations. The amount of metals emitted by the volcano appeared to be decreasing over the years following the eruption in 2011-2012, which greatly reduced the biomass of the plankton living in the area of influence of the volcano. In 2013 the metal concentrations found in the plankton living in the area were very high, but a decrease in concentrations was found towards 2016. Around the volcano the metal concentrations in the plankton were significantly higher than at the reference stations, just like in the seawater, except for 2016, which showed significantly lower concentrations. The increase in metal concentrations due to the volcano was comparable to increases in concentrations due to anthropogenic pollution in other studies. The decrease in concentrations in 2016 could be attributed to the strong increase in biomass of the plankton, induced by the large amounts of nutrients and Fe(II) emitted by the volcano. It is most likely that the high concentrations of toxic metals caused DNA damage in the plankton and that these metals were tranferred up in the foodchain. But as the concentrations have diminished greatly, they do not seem to pose a hazard anymore in 2016. It appears that the ecosystem, after being strongly damaged and intoxicated by metals from the volcano, was able to recover using elements emitted by the same volcano.

Chapter 1

Introduction

1.1 Background

In the Marine Reserve of El Hierro island (Canary Islands, Spain, Fig. 1.1), a submarine volcanic eruption took place 1.8 km south of La Restinga village in October 2011. During the next 6 months, extreme physical-chemical perturbations were caused by this event, comprising of thermal changes, water acidification, deoxygenation and metal-enrichment, which resulted in significant alterations of the marine ecosystem (Fraile-Nuez et al. [2012], Santana-Casiano et al. [2013]). After March 2012, once the eruptive phase was finished, the submarine volcano, named Tagoro, became a hydrothermal vent system with an active degasification phase involving the release of heat, gases and metals. Nowadays this system still produces significant physical-chemical anomalies in the surrounding waters, like the discharge of CO_2 which greatly increases global CO_2 flux and increases the acidity of the seawater above the volcano by about 20% (Santana-Casiano et al. [2016], Fraile-Nuez et al. [2016]). The fluids emitted by these kind of vents, are known to contain high concentrations of metals (Schmidt et al. [2011]) and attribute to an elevated metal content (Sander and Koschinsky [2011]).

First level organisms, like phytoplankton, passively adsorb and actively assimilate metals, introducing them into the marine food chain (González-Dávila [1995], Jakimska et al. [2011]). The adsorbed metals, like Pb and Cd, are not used by the organism and can be toxic, inhibiting growth, even at low concentrations (Sunda [1989]). Other metals assimilated by the organisms are essential micronutrients and are used in different enzymatic reactions. These include Cu, Zn, Fe, Cr and Co (Whitfield [2001]), but at certain concentration levels these metals may also become toxic to the organisms living in the seawater (Jakimska et al. [2011], Goswami et al. [2014]). The effect of biomagnification, which increases the concentration per step in the food chain, can eventually create a risk to human health at the end of the chain (Chen et al. [2000], Jrup [2003], Rubio-Franchini et al. [2008], Arnot et al. [2010]).

Several studies have been carried out in order to study the influence and accumulation of metals on plankton. These metals were often introduced by anthropogenic sources and most of these studies examined freshwater (Brügmann and Hennings [1994], Chen et al. [2000], Rejomon and JOSEPH [2008], Rossi and Jamet [2008], [Atici et al., 2010],Bahnasawy et al. [2011], Hammerschmidt et al. [2013], Battuello et al. [2016]). Leoni and Garibaldi [2009] looked at the influence of high metal concentrations on plankton in a volcanic lake, concluding that the metals interfere with the prey-predator system in the plankton community. Khristoforova et al. [2015], with the study of the salmon, found a relation between elevated concentrations of metals in the food chain and volcanic activity. Elevated metal concentrations in plankton due to a submarine volcano were found in Antarctica in an area well protected from the open ocean (Deheyn et al. [2005]). Nevertheless, studies on active submarine volcanoes are sparse.

The present study investigates, for the first time, the accumulation and influence of metals on an open ocean plankton community affected by a very young active shallow submarine volcano in a degasification phase. In this research, the concentrations of twenty different metals were quantified in plankton and in seawater samples collected during four different cruises from 2013-2016. With these concentrations can be determined whether the volcano Tagoro emitted metals in any significant proportion and if the plankton in the area and above the volcano accumulate these metals. By comparing these possibly elevated concentrations with each other and to previous studies, the potential impact on the environment can be assessed.

1.2 Research area

The submarine volcano Tagoro is located 1.8 km South of La Restinga village on the island El Hierro (Fig. 1.1)(27°37.221' N and 17°59.605' W). El Hierro is the youngest island of the Canary Archipelago (1.12 million years old), which was created by the movement of the African continental plate from west to east over a hot spot (Guillou et al. [1996], Carracedo et al. [2002], Zaczek et al. [2015]). In October 2011 the submarine eruption started and the evolution of the volcano has been monitored since by at least two cruises each year performed within the framework of the Vulcano and Vulcana projects lead by the Spanish Institute of Oceanography. As mentioned before, the eruption caused extreme physical-chemical perturbations to the seawater (Fraile-Nuez et al. [2012], Santana-Casiano et al. [2013]), which spread over the entire area and can be seen in the satellite pictures shown in figure 1.2.

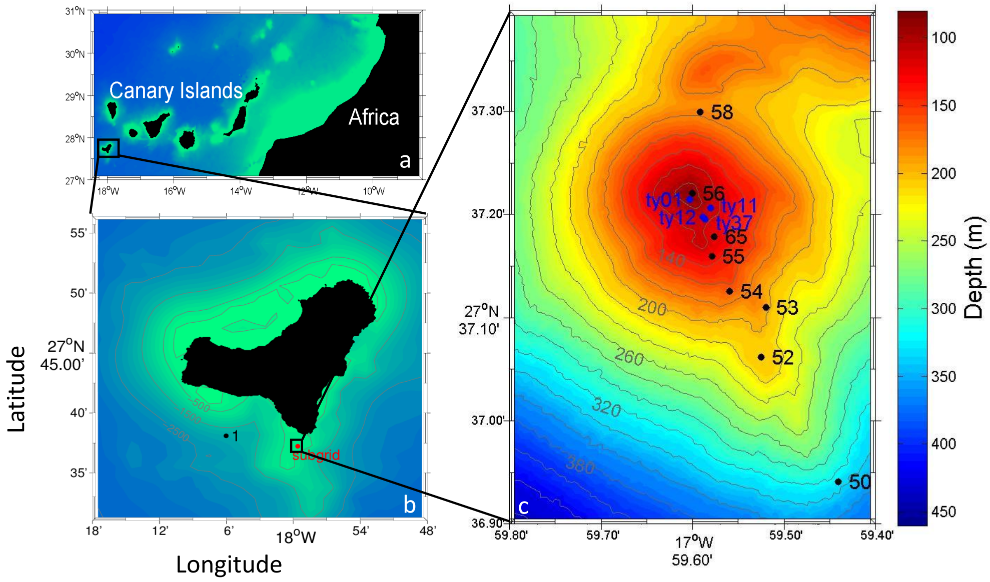
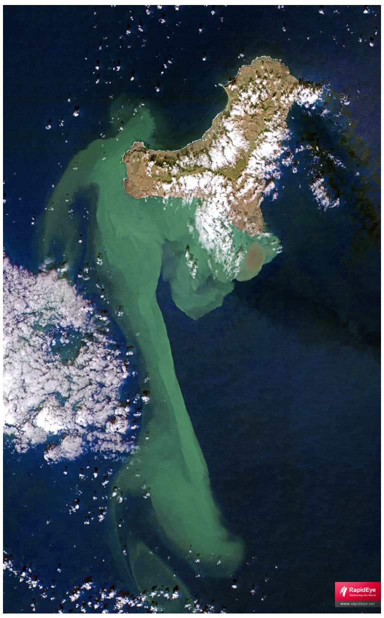
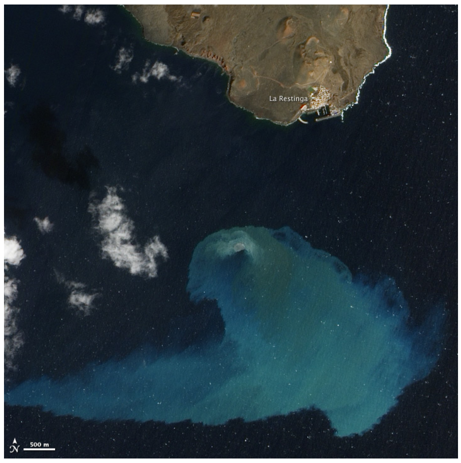


Figure 1.1: a) Canary Archipelago and West-Africa. The black rectangle localizes the island of El Hierro, where the submarine volcano Tagoro is located. b) El Hierro with reference station 1 and the location of the volcano Tagoro. c) Subgrid to show the detail of the research above the volcano. Distances between stations are roughly 40-120 m. Station 56 is located over the main crater.



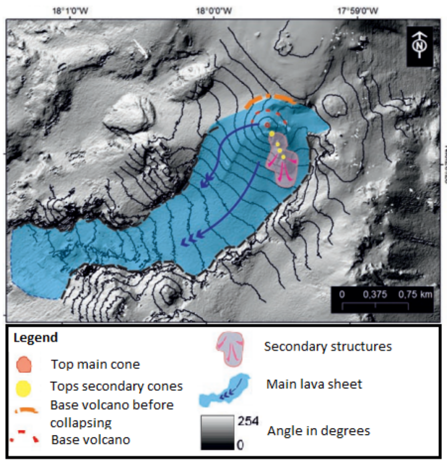
(a) 26 October 2011 by RapidEye.



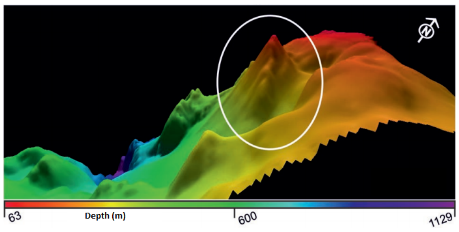
(b) 1 April 2012. NASA Earth Observatory image by Jesse Allen and Robert Simmon, using EO-1 ALI data.

Figure 1.2: Satellite images of two different moments during the eruption of the volcano Tagoro. The location of the volcano is given in figure 1.1.

The volcano Tagoro is 312 m high compared to the situation before the eruption with the main cone at a depth of 88 m from the surface (Fraile-Nuez et al. [2015]). It grew in a pre-existing valley in the western flank of the southern ridge of El Hierro. Several secondary cones follow the main direction of this ridge South-East of the main cone (Fig. 1.3a, Fig. 1.3b). This ridge is one of El Hierros volcanic rift zones defined by fissuring, faulting, and aligned eruptive centers. The fissural type of eruption of the volcano Tagoro corresponds well with this definition of the area (Carracedo [1994], Rivera et al. [2014]). The main flow of lava was through a submarine valley West-South-West of the volcano, which directed the lava flow toward an archipelagic apron at depths over 1000 m. During the eruptive phase, when the volcano was growing, the structure collapsed twice (Rivera et al. [2013]).



(a) Morphology of the volcano (Fraile-Nuez et al. [2015]).



(b) View of the volcano in 3d with the main cone and smaller secondary cones (Fraile-Nuez et al. [2015]).

Figure 1.3: Structure of the volcano Tagoro South of the island El Hierro, as shown in figure 1.1.

The seawater and plankton around the volcano Tagoro are being transported laterally by two types of currents, a large scale ocean current and local varying wind-driven currents. The metal concentration in the seawater is less affected than the plankton by these currents, as the metals are emitted by hydrothermal vents on the oceanfloor, whilst the plankton live near the surface, where conditions are most favourable.

The oceanic dynamic of the area is characterized by the presence of the Canary Current with a predominant flow to the South-west. North Atlantic Central Water, which is characterized by a straight line in temperature(θ)/salinity(S) from 0-700 m depth, flows southward in the upper levels with a mean mass transport of -2.2 ± 0.90 Sv. The intermediate level waters are characterized by seasonal flow reversals with a northward progression of Antarctic Intermediate Water from July to October followed by an intense flow reversal of Mediterranean Water in November and December (Hernández-Guerra et al. [2002], Hernández-Guerra et al. [2003], Hernández-Guerra et al. [2005], Fraile-Nuez and Hernández-Guerra [2006], Machín and Pelegrí [2006], Machín et al. [2006], Fraile-Nuez et al. [2010], Machín et al. [2010], Pastor et al. [2015]). The area is dominated by the trade winds from the North-east, producing areas of low wind intensity in the South of the islands. In March 2013 the area had an anomalous wind pattern with wind coming primarily from the West. Figures 1.4, 1.5, 1.6 and 1.7 show the wind directions and velocities as calculated by the SIMAR model during the months of the monitoring cruises in three different locations around the volcano Tagoro.

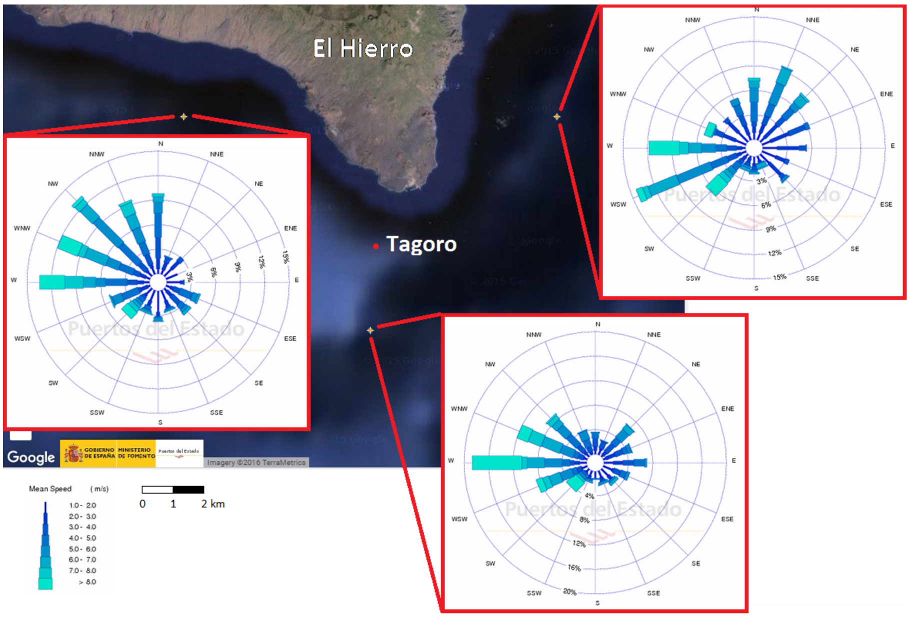


Figure 1.4: Windroses containing the wind direction and velocity for March 2013 in three locations around the volcano Tagoro South of the island El Hierro, as shown in figure 1.1. The values were calculated by the SIMAR model and generated by Puertos del Estado of the Spanish government.

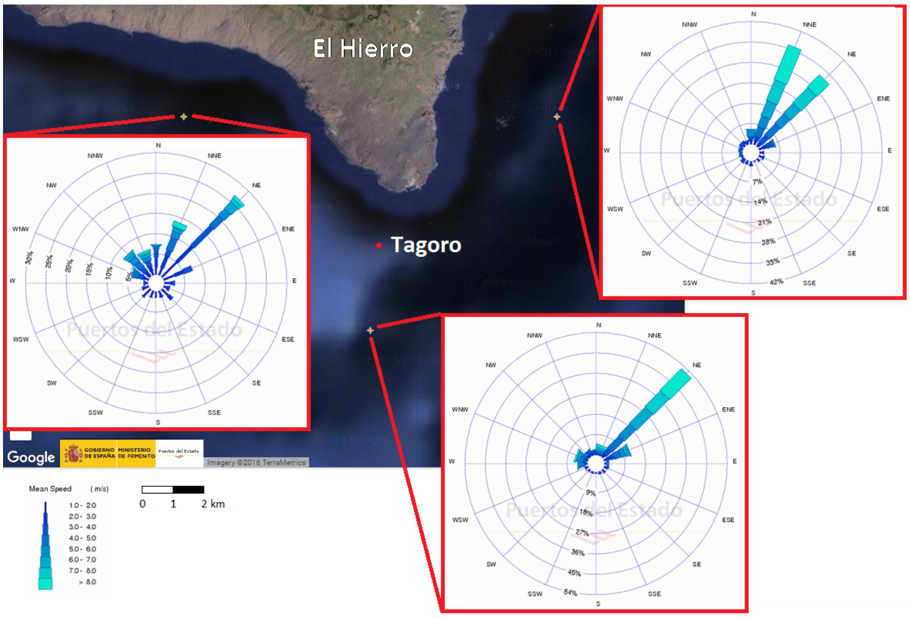


Figure 1.5: Windroses containing the wind direction and velocity for October 2013 in three locations around the volcano Tagoro South of the island El Hierro, as shown in figure 1.1. The values were calculated by the SIMAR model and generated by Puertos del Estado of the Spanish government.

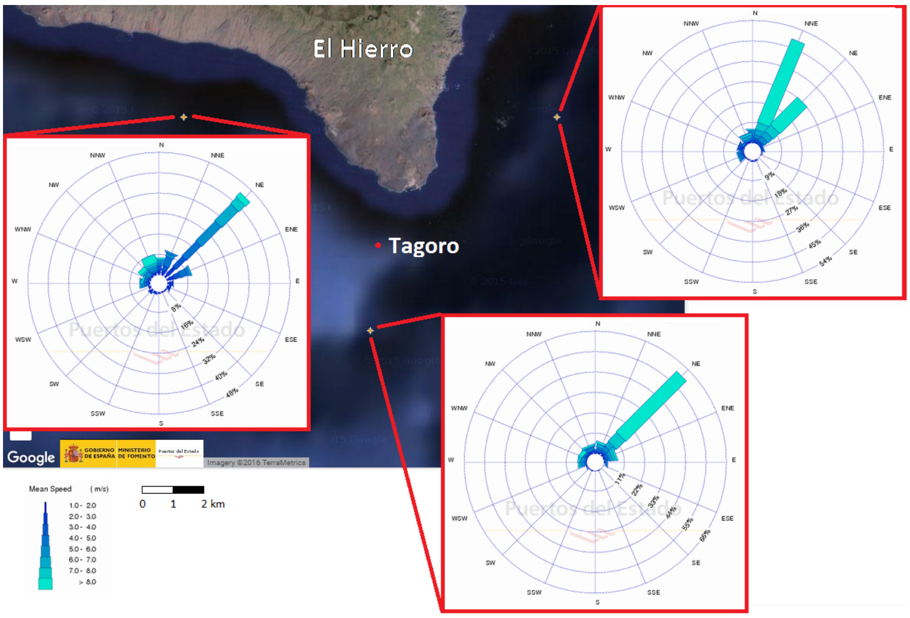


Figure 1.6: Windroses containing the wind direction and velocity for March 2014 in three locations around the volcano Tagoro South of the island El Hierro, as shown in figure 1.1. The values were calculated by the SIMAR model and generated by Puertos del Estado of the Spanish government.

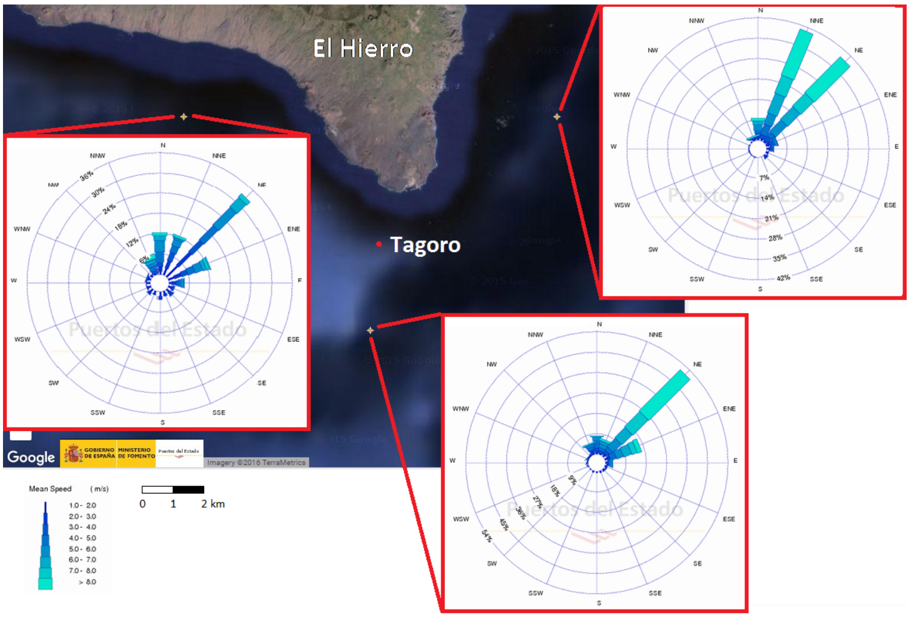


Figure 1.7: Windroses containing the wind direction and velocity for March 2016 in three locations around the volcano Tagoro South of the island El Hierro, as shown in figure 1.1. The values were calculated by the SIMAR model and generated by Puertos del Estado of the Spanish government.

Chapter 2

Data and Methods

In order to quantify the metal content, samples of seawater and plankton were collected during four monitoring cruises of which the author participated in the most recent (Table 2.1). The samples, both seawater and plankton, were first prepared in the laboratory, so that the metal concentrations could be measured with a spectrometer, after which the obtained values could be processed.

Table 2.1: Dates of the monitoring cruises during which seawater and plankton samples were collected around the volcano Tagoro South of the island El Hierro, as shown in figure 1.1.

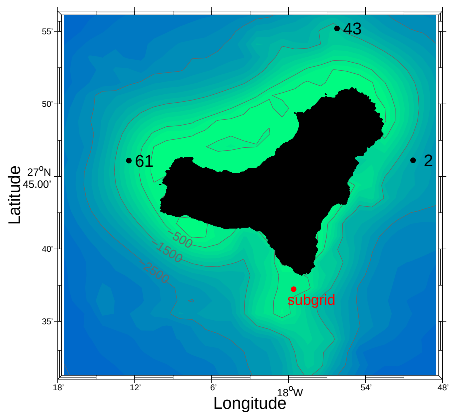
Project	Cruise	Start date (dd-mm-yyyy)	End date (dd-mm-yyyy)
Vulcano	Vulcano0313	20-03-2013	04-04-2013
	Vulcano1013	26-10-2013	10-11-2013
	Vulcano0314	08-03-2014	23-03-2014
Vulcana	Vulcana0316	07-03-2016	17-03-2016

2.1 Seawater sampling

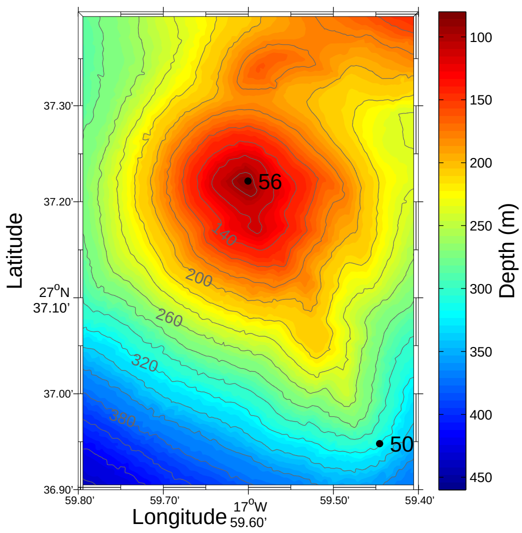
The locations of the hydrothermal vents emitting the metals were found by carrying out several tow-yos during the Vulcano and Vulcana projects using a Seabird 911 + CTD with pH sensor (Santana-Casiano et al. [2016], Fraile-Nuez et al. [2016]). With the CTD (Conductivity, Temperature and Depth device) the temperature, salinity, oxygen content and chlorophyll-a content in the seawater were measured.

Water samples were obtained using a rosette of 24 10-liter Niskin bottles. No duplicate samples could be taken. During the four different cruises a total of 208 seawater samples were taken at several depths in the water column in order to measure the metal content. During these cruises, 34, 50, 48 and 50 water samples from 5, 8, 11 and 13 stations were collected, respectively (Tab. 2.2). For every cruise at least one station outside of the volcanic area was sampled as a reference station (Fig. 2.1, 2.2, 2.3 and 2.4).

In order to preserve the state of the metals and reduce the contamination of the water samples, Patterson and Settle [1976] methodology was followed. Moreover, sterilized bags were put around the bottles and exposure time of the water sample to airborne particles was minimized in order to reduce possible contamination. The rosette may produce a metal contamination of the water samples. In order to quantify this possible contamination, Go-Flo bottles, which are completely metal free, were used during the first cruise of the Vulcano project (Vulcano0313) at several stations and depths and these samples were compared to the samples taken with the rosette. Water samples were acidified with a few drops of 65% HNO_3 in a total volume bottle of 2 litres.



(a) Reference stations around the island El Hierro, Canary Islands.



(b) Subgrid with the stations around the volcano Tagoro.

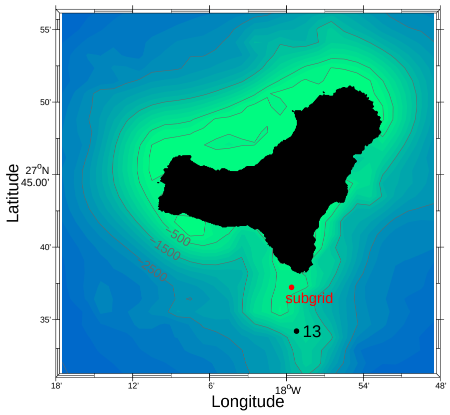
Figure 2.1: Locations of the stations where seawater samples were taken during the Vulcano0313 cruise in order to measure the metal content.

Table 2.2: Station locations, depths and sampling dates of the monitoring cruises (Tab. 2.1), where seawater samples were taken in order to measure the metal content.

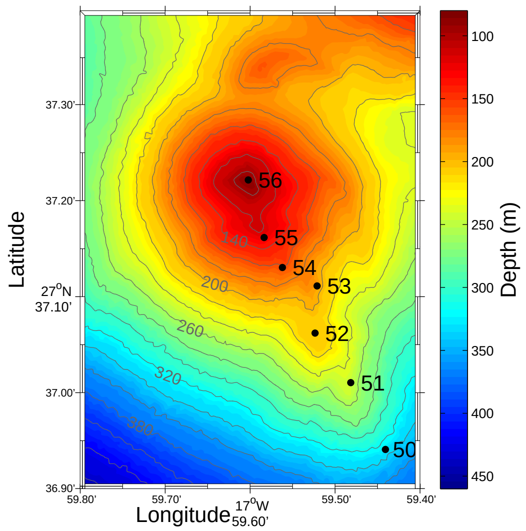
Cruise	Station	Date (dd-mm-yy hh:mm)	Latitude (°)	Longitude (°)	Depth (m)
Vulcano0313	2	27-03-13 10:11	27.7686	-17.8382	1394
	43	5-04-13 14:52	27.9200	-17.9370	1827
	50	29-03-13 8:06	27.6158	-17.9908	324
	56	29-03-13 18:22	27.6204	-17.9933	90
	61	2-04-13 7:30	27.7682	-18.2074	1247
Vulcano1013	13	2-11-13 18:06	27.5700	-17.9870	1039
	50	3-11-13 7:13	27.6157	-17.9907	291
	51	3-11-13 8:51	27.6168	-17.9914	241
	52	3-11-13 10:16	27.6177	-17.9921	205
	53	3-11-13 11:49	27.6185	-17.9920	187
	54	3-11-13 12:56	27.6188	-17.9927	154
	55	3-11-13 20:30	27.6194	-17.9931	120
	56	3-11-13 15:25	27.6204	-17.9934	93
Vulcano0314	13	12-03-14 10:45	27.5698	-17.9872	1039
	50	17-03-14 8:04	27.6156	-17.9907	299
	51	17-03-14 9:22	27.6168	-17.9913	237
	52	17-03-14 10:16	27.6177	-17.9920	202
	53	17-03-14 11:16	27.6185	-17.9921	183
	54	17-03-14 12:14	27.6188	-17.9927	154
	55	17-03-14 13:02	27.6193	-17.9930	122
	56	17-03-14 13:45	27.6203	-17.9933	93
	58	17-03-14 14:28	27.6217	-17.9932	175
	59	17-03-14 15:22	27.6222	-17.9930	166
	61	17-03-14 19:30	27.6196	-17.9932	117
Vulcana0316	1	10-03-16 9:09	27.6349	-18.1004	1200
	50	10-03-16 11:40	27.6157	-17.9907	346
	52	10-03-16 13:17	27.6177	-17.9921	216
	53	11-03-16 14:31	27.6185	-17.9920	206
	54	11-03-16 15:47	27.6188	-17.9927	156
	55	11-03-16 16:47	27.6193	-17.9930	126
	56	11-03-16 21:02	27.6203	-17.9933	96
	58	11-03-16 22:38	27.6217	-17.9932	176
	65	11-03-16 18:16	27.6196	-17.9929	136
	TY01*	12-03-16 10:26	27.6202	-17.9934	289
	TY11*	12-03-16 19:11	27.6201	-17.9930	134
	TY12*	12-03-16 19:57	27.6200	-17.9931	134
	TY37*[1]	15-03-16 17:17	27.6199	-17.9931	136

* Samples taken during Tow-Yos. The Niskin bottle was closed when the pH sensor showed high anomalies, compared to the values outside of the volcanically active area,

[1] Sample taken from a horizontally placed Niskin bottle at the bottom of the rosette to get closer to the ocean floor.

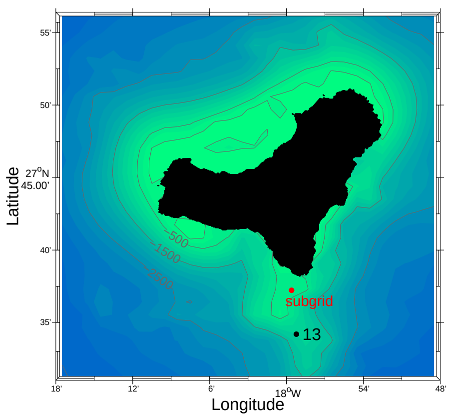


(a) Reference station near the island El Hierro, Canary Islands.

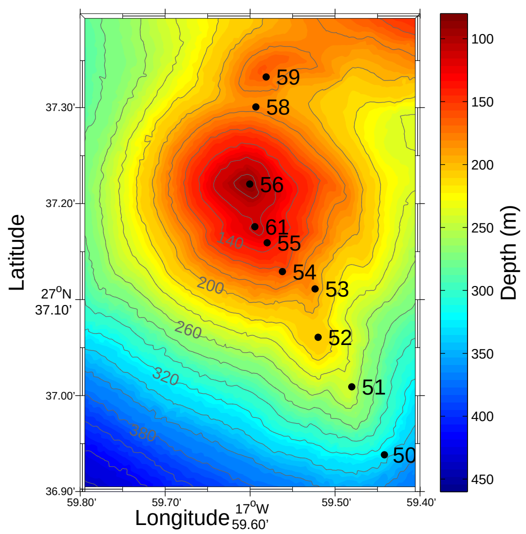


(b) Subgrid with the stations around the volcano Tagoro.

Figure 2.2: Locations of the stations where seawater samples were taken during the Vulcano1013 cruise in order to measure the metal content.

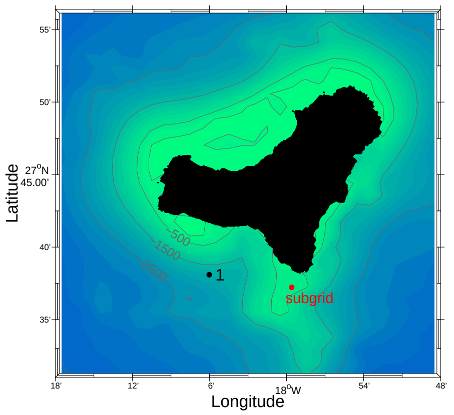


(a) Reference station near the island El Hierro, Canary Islands.

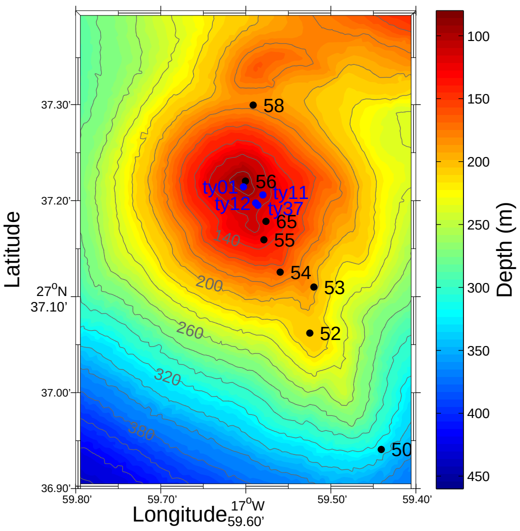


(b) Subgrid with the stations around the volcano Tagoro.

Figure 2.3: Locations of the stations where seawater samples were taken during the Vulcano0314 cruise in order to measure the metal content.



(a) Reference station near the island El Hierro, Canary Islands.



(b) Subgrid with the stations around the volcano Tagoro.

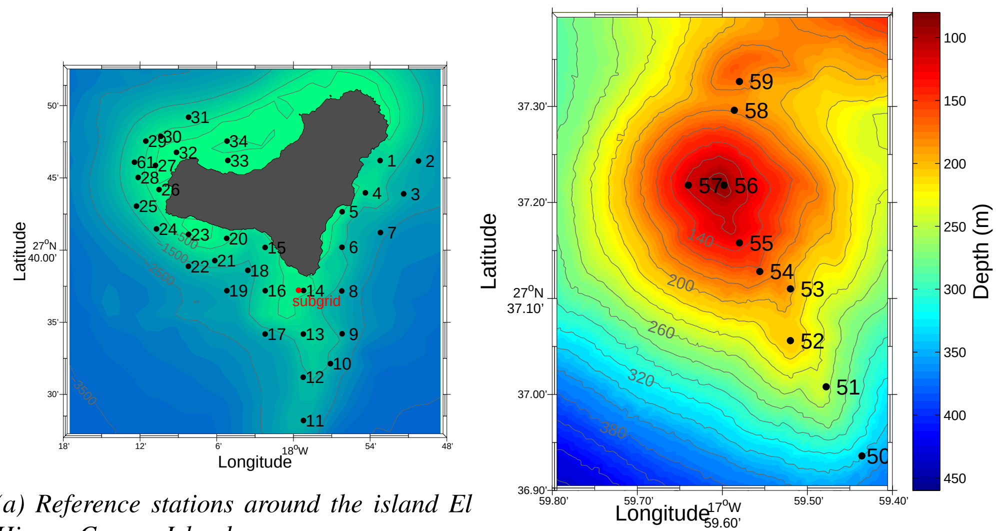
Figure 2.4: Locations of the stations where seawater samples were taken during the Vulcana0316 cruise in order to measure the metal content.

At the laboratory, empty porcelain sample cups were sterilized at 800 °C for 2 hours using a muffle oven. Volumes of 50 mL seawater sample were added to the cups which were placed in an oven at 60 °C for 48 hours. The dried samples, consisting of salt, were then acidified with a few drops of 65% HNO_3 after which they were placed on a hotplate to evaporate the acid. In order to break apart any organic matter, the samples were incinerated at 450 °C for 24 h using a muffle oven. The calcined samples were then prepared for measuring the metal content with the spectrometer by diluting them using 50 mL 1.5% HNO_3 (Sec. 2.3).

2.2 Plankton sampling

Plankton was sampled vertically using a WP2 net with a diameter of 57 cm and a mesh size of 200 μm (UNESCO [1968]). The net was towed to the surface from a depth of 200 m or the bottom if it was more shallow. A total of 81 plankton samples were taken from three different cruises (Vulcano0313, Vulcano1013 and Vulcana0316) to measure the biomass and the metal content (Tab. 2.3 and 2.4). During these cruises samples were collected from 45, 23 and 13 different stations, respectively (Fig. 2.5, 2.6 and 2.7). The plankton were frozen directly after being sampled.

At the laboratory the plankton samples were analysed after being unfrozen. Filter paper was used to drain the water from the plankton samples, which were then added to porcelain sample cups, which had been sterilized at 800 °C for 2 hours using a muffle oven. After drying the samples at 70 °C for 24 h, the dry weight (m_{dry}) of the plankton was obtained using a scale with a precision of 1 mg. The samples were then acidified with a few drops of 65% HNO_3 and placed on a hotplate to evaporate the nitric acid. In order to break apart the organic matter, the samples were incinerated at 450 °C for 24 h using a muffle oven. This process of acidification and incineration was repeated until all organic matter was broken down. The samples were then prepared for measuring the metal content with the spectrometer by diluting them using 25 mL 1.5% HNO_3 (Sec. 2.3).



(a) Reference stations around the island El Hierro, Canary Islands.

(b) Subgrid with the stations around the volcano Tagoro.

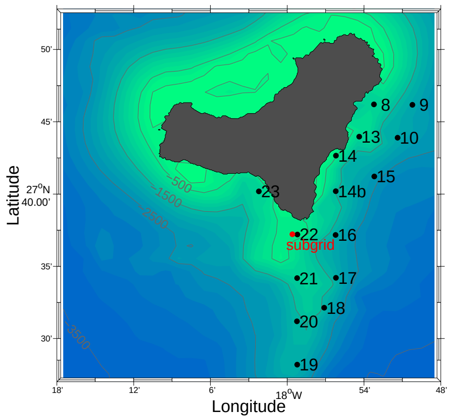
Figure 2.5: Locations of the stations where plankton samples were taken during the Vulcano0313 cruise in order to measure the metal content.

Table 2.3: Station locations, net depths and sampling dates of the monitoring cruise Vulcano0313 (Tab. 2.1), where plankton samples were taken in order to measure the metal content.

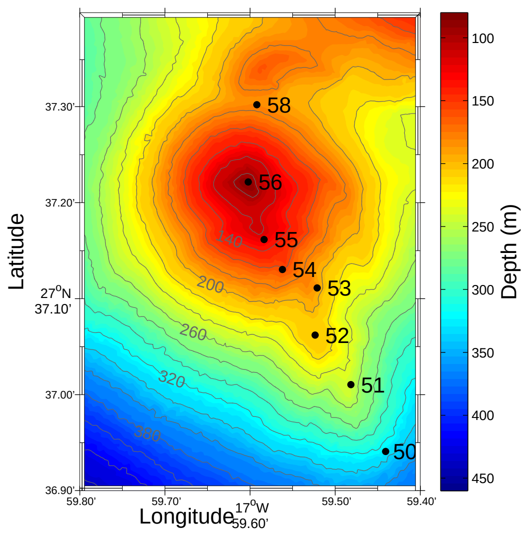
Cruise	Station	Date (dd-mm-yy hh:mm)	Latitude (°)	Longitude (°)	Depth WP2 (m)
Vulcano0313	1	27-03-13 15:23	27.7700	-17.8871	200
	2	27-03-13 10:11	27.7695	-17.8370	200
	3	27-03-13 12:48	27.7316	-17.8563	200
	4	27-03-13 17:39	27.7328	-17.9063	200
	5	27-03-13 20:35	27.7110	-17.9366	200
	6	27-03-13 22:09	27.6700	-17.9368	200
	7	28-03-13 8:13	27.6870	-17.8866	200
	8	28-03-13 10:51	27.6195	-17.9370	200
	9	28-03-13 13:05	27.5701	-17.9366	200
	10	28-03-13 15:21	27.5355	-17.9518	200
	11	28-03-13 17:13	27.4698	-17.9870	200
	12	28-03-13 19:32	27.5198	-17.9873	200
	13	28-03-13 21:25	27.5698	-17.9871	200
	14	30-03-13 11:26	27.6200	-17.9868	200
	15	30-03-13 12:44	27.6698	-18.0370	200
	16	31-03-13 7:11	27.6198	-18.0368	200
	17	30-03-13 14:24	27.5698	-18.0370	200
	18	31-03-13 13:54	27.6433	-18.0595	200
	19	31-03-13 15:53	27.6198	-18.0868	200
	20	31-03-13 18:27	27.6803	-18.0870	200
	21	31-03-13 19:51	27.6546	-18.1025	200
	22	1-04-13 7:09	27.6480	-18.1370	200
	23	1-04-13 9:25	27.6848	-18.1368	200
	24	1-04-13 11:58	27.6911	-18.1786	200
	25	1-04-13 13:50	27.7175	-18.2046	200
	26	1-04-13 16:20	27.7366	-18.1753	200
	27	1-04-13 18:04	27.7645	-18.1800	200
	28	1-04-13 20:28	27.7505	-18.2025	200
	29	2-04-13 9:00	27.7925	-18.1925	200
	30	2-04-13 11:00	27.7980	-18.1730	200
	31	2-04-13 16:06	27.8200	-18.1368	200
	32	2-04-13 18:53	27.7795	-18.1525	200
	33	2-04-13 20:32	27.7701	-18.0855	200
	34	3-04-13 7:50	27.7925	-18.0866	200
	50	29-03-13 8:06	27.6156	-17.9906	200
	51	29-03-13 10:20	27.6168	-17.9913	200
	52	29-03-13 11:42	27.6176	-17.9920	180
	53	29-03-13 13:30	27.6185	-17.9920	160
	54	29-03-13 15:38	27.6188	-17.9926	130
	55	29-03-13 17:27	27.6193	-17.9930	100
	56	29-03-13 18:22	27.6203	-17.9933	80
	57	29-03-13 19:30	27.6203	-17.9940	100
	58	30-03-13 8:45	27.6216	-17.9931	200
	59	30-03-13 10:00	27.6221	-17.9930	150
	61	2-04-13 7:30	27.7681	-18.2073	200

Table 2.4: Station locations, net depths and sampling dates of the monitoring cruises Vulcano1013 and Vulcana0316 (Tab. 2.1), where plankton samples were taken in order to measure the metal content.

Cruise	Station	Date (dd-mm-yy hh:mm)	Latitude (°)	Longitude (°)	Depth WP2 (m)
Vulcano1013	8	7-11-13 10:05	27.7700	-17.8871	200
	9	7-11-13 11:38	27.7695	-17.8370	200
	10	7-11-13 13:39	27.7316	-17.8563	200
	13	2-11-13 18:06	27.7328	-17.9063	200
	14	2-11-13 20:20	27.7110	-17.9366	200
	14b	2-11-13 20:55	27.6700	-17.9368	200
	15	2-11-13 12:23	27.6870	-17.8866	200
	16	2-11-13 13:36	27.6195	-17.9370	200
	17	2-11-13 15:36	27.5701	-17.9366	200
	18	2-11-13 9:36	27.5355	-17.9518	200
	19	2-11-13 7:03	27.4698	-17.9870	200
	20	1-11-13 22:05	27.5198	-17.9873	200
	21	1-11-13 19:11	27.5698	-17.9871	200
	22	1-11-13 16:28	27.6200	-17.9868	200
	23	1-11-13 12:30	27.6698	-18.0370	200
	50	3-11-13 7:13	27.6157	-17.9907	200
	51	3-11-13 8:51	27.6168	-17.9914	200
	52	3-11-13 10:16	27.6177	-17.9921	175
	53	3-11-13 11:49	27.6185	-17.9920	170
	54	3-11-13 12:56	27.6188	-17.9927	145
	55	3-11-13 20:30	27.6194	-17.9931	120
	56	3-11-13 15:25	27.6204	-17.9934	85
	58	3-11-13 16:37	27.6217	-17.9932	165
Vulcana0316	1	10-03-16 10:30	27.6349	-18.1004	200
	50	10-03-16 12:02	27.6157	-17.9907	200
	51	11-03-16 13:56	27.6169	-17.9913	200
	52	10-03-16 13:53	27.6177	-17.9921	200
	53	11-03-16 14:59	27.6185	-17.9920	200
	54	11-03-16 16:16	27.6188	-17.9927	170
	55	11-03-16 17:13	27.6193	-17.9930	145
	56	11-03-16 0:00	27.6203	-17.9933	90
	57	11-03-16 22:02	27.6210	-17.9933	129
	58	11-03-16 23:03	27.6217	-17.9932	170
	59	11-03-16 23:48	27.6222	-17.9930	170
	61	11-03-16 17:57	27.6195	-17.9932	118
	65	11-03-16 18:36	27.6197	-17.9930	128

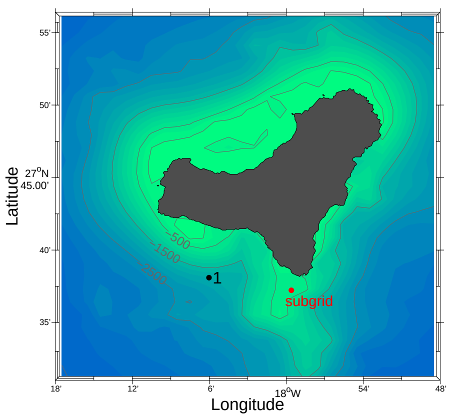


(a) Reference stations around the island El Hierro, Canary Islands.

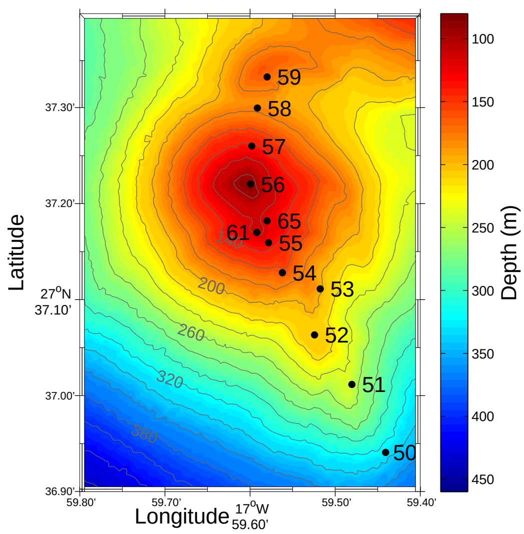


(b) Subgrid with the stations around the volcano Tagoro.

Figure 2.6: Locations of the stations where plankton samples were taken during the Vulcano1013 cruise in order to measure the metal content.



(a) Reference station near the island El Hierro, Canary Islands.



(b) Subgrid with the stations around the volcano Tagoro.

Figure 2.7: Locations of the stations where plankton samples were taken during the Vulcana0316 cruise in order to measure the metal content.

2.3 Spectrometry

Metal content of both the seawater and plankton samples was analysed using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), which is an approved method for the quantification of metals Lee and Cunniff [1995]. The Thermo Scientific iCAP 6000 series spectrometer of the Public Health Lab was used to do this (Santa Cruz de Tenerife, Spain). The programmed conditions of ICP-OES for metal determination were as follows: gas flow (nebulization gas flow, auxiliary gas flow) 0.5 l/min, approximate RF power 1200 W, stabilization time 0 s, samples injection pump flow 50 rpm (stabilization flow, analysis flow).

Instrumental detection and quantification limits were estimated based on the response of the equipment. The limits were determined by analysing 15 blanks in conditions of reproducibility (Currie [1995]). Instrumental detection and quantification limits are shown in table 2.5 with the wavelengths at which they were determined.

Results below the detection limit of the spectrometer were changed to no available number (NaN) for further calculation. Na concentration was recalculated with a conversion factor of 10 for the seawater samples, as the concentrations were too high for the calibration curve of the spectrometer.

Table 2.5: Instrumental detection and quantification limits of the spectrometer used to measure the metal content in the seawater and plankton.

Metal	wavelength (nm)	Detection limit (mg/l)	Quantification limit (mg/l)
Al	167.0 nm	0.004	0.012
B	249.7 nm	0.003	0.012
Ba	455.4 nm	0.001	0.005
Ca	317.9 nm	0.58	1.955
Cd	226.5 nm	0.0003	0.001
Co	228.6 nm	0.0006	0.002
Cr	267.7 nm	0.003	0.008
Cu	327.3 nm	0.004	0.012
Fe	259.9 nm	0.003	0.009
K	769.9 nm	0.565	1.884
Li	670.8 nm	0.005	0.013
Mg	279.1 nm	0.583	1.943
Mn	257.6 nm	0.002	0.008
Mo	202.0 nm	0.0007	0.002
Na	589.6 nm	1.097	3.655
Ni	231.6 nm	0.0007	0.003
Pb	220.3 nm	0.0003	0.001
Sr	407.7 nm	0.0007	0.003
V	310.2 nm	0.001	0.005
Zn	206.2 nm	0.002	0.007

2.4 Bathymetry

Two datasets of bathymetry, submarine topography, data were used to create the maps: *Topo15.1* created by Smith and Sandwell [1997] to create the overview of the island (Fig. 1.1a,b) and a multi-beam bathymetry dataset obtained during the Vulcano0314 cruise to create maps of the volcano, which is not presented yet in the global database (Fig. 1.1c). The bathymetric data of the monitoring cruise was acquired using a Konsberg Simrad EM-710 echosounder, which operates at sonar frequencies in the 70 to 100 kHz range, the data was processed with CARIS HIPS and SIPS and yields a bathymetric grid resolution of 5 m with 100% coverage (AMPLIAR).

2.5 Data Analysis

All data was processed and analysed using the software MATLAB (MATLAB [2013]). Results below the detection limit of the spectrometer and also possible erroneous results due to contamination were removed by carrying out a quality control. This control was done by looking at the vertical profiles of the metal concentrations and values completely out of line with the the surrounding concentrations (extreme values) were considered erroneous. The latter could however not be checked statistically as no duplicate samples could be taken. For the reference stations the shapes of the vertical metal concentrations profiles were also compared to previous studies (Bruland [1980], Bruland and Franks [1983], Pohl et al. [1993], Bruland et al. [1994], de Villiers and Nelson [1999], Morel and Price [2003] and Pohl et al. [2011]). The data was interpolated using linear interpolation.

2.5.1 Conservative metal concentrations

The Marcet equation was used to calculate concentrations of several metals (Sr, Ca, K, Mg and Na) for conservative seawater to compare with the obtained concentrations of the seawater samples (Eq. 2.1 and 2.2, F.I. Millero, Chemical Oceanography, 2013):

$$Cl = \frac{Sal}{1.80655} \tag{2.1}$$

$$M_n = Cl \cdot (n/Cl)_{standard} \tag{2.2}$$

where Cl = is the concentration of Chloride in g/kg
Sal = Salinity, measured with the CTD
M_n = concentration of metal *n* in g/kg
$(n/Cl)_{standard}$ = is the weight percentage of metal *n* compared to Chloride for standard seawater. Values used are 0.556614 for Na^{+}, 0.06626 for Mg^{2+}, 0.02127 for Ca^{2+}, 0.0206 for K^{+} and 0.00041 for Sr^{2+}.

2.5.2 Biomass

The biomass, dry weight, of the plankton was divided by the volume that passed through the WP2 net. But because most of the plankton lives in the upper 100 m of the ocean, where the conditions for growth are most favourable, the biomass of the plankton in mg/m^3 was normalized for the depth (Eq. 2.3, Stemmann et al. [2007], Gaard et al. [2008] and Palomares-García et al. [2013]). In this way, any differences in biomass concentration caused by differences in the depth of sampling were taken away.

$$m_{dry}(mg/m^2) = m_{dry}(mg/m^3) \cdot depth(m) \tag{2.3}$$

2.5.3 Bioconcentration factors

For each metal element bioconcentration factors (BCFs) were calculated. This was done by dividing the metal concentration in the dried plankton by the metal concentration in the surrounding seawater (Eq. 2.4). The BCF is a ratio to show how much of a substance is accumulated by an organism living in the medium containing the substance.

$$BCF(L/kg) = \frac{Concentration_{plankton}(mg/kg_{dry})}{Concentration_{seawater}(mg/L)} \tag{2.4}$$

Chapter 3

Results and Discussion

To investigate whether the volcano influenced the metal concentrations in the seawater and the amount of metals accumulated by the plankton, the arithmetic means were calculated of the concentrations at the reference stations and of all stations around the volcano. The many stations around the volcano allowed for the calculation of standard deviations, which made it possible to determine which values were significantly different around the volcano compared to the reference stations.

3.1 Seawater

Appendix A presents the results of the seawater analysis in tables A.1, A.2, A.3 and A.4 for cruises Vulcano0313, Vulcano1013, Vulcano0314 and Vulcana0316, respectively. First the two different methods for seawater sampling are compared, after which the metal content in the seawater samples is discussed.

3.1.1 Method comparison

To determine if a rosette with Niskin bottles is an appropriate method to obtain seawater samples for the measurement of metal concentrations, a comparison between the two different methodologies, Go-Flo and rosette, is shown in figure 3.1. It shows a strong relation with a significance level (α) of 0.02 resulting in a coefficient of determination (R^2) of 0.999 when using all the comparable elements and 0.989 when zooming in on the elements with the lowest concentrations. This means that for this study water samples obtained by the rosette (tables A.1, A.2, A.3 and A.4) can be considered as reliable as the metal-free Go-Flo water samples.

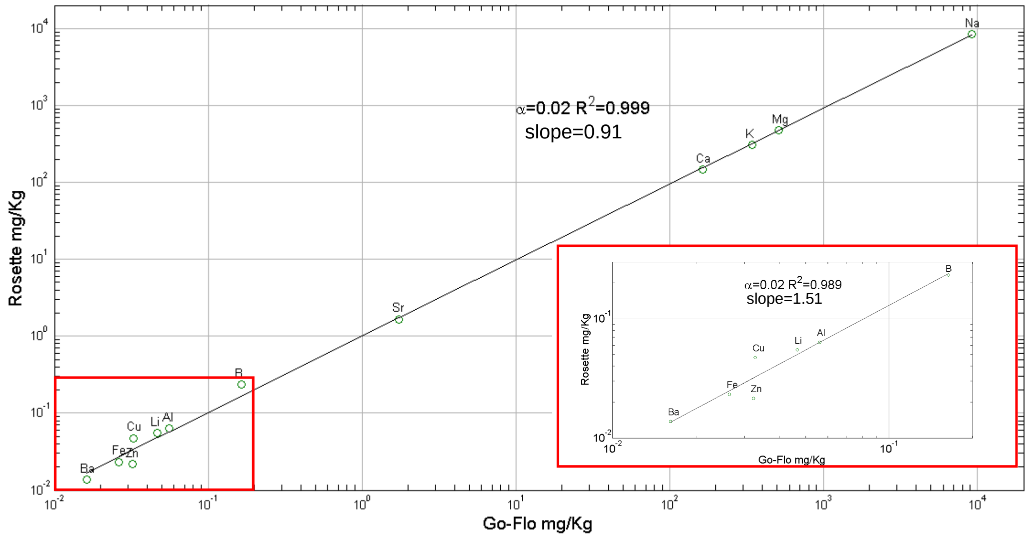


Figure 3.1: Comparison between mean concentrations of each metal element for the samples obtained with the Go-Flo (metal-free bottle) and rosette methods at station 61 (Fig.2.1a at Vulcano0313).

3.1.2 Seawater metal content

The mean concentrations of each metal element at all reference stations in the seawater column up to 200 m depth are shown in figure 3.2a with Vulcano0313 being represented by an average of the three reference stations sampled (st. 2, 43 and 61 fig. 2.1a). An average of all reference stations sampled in March (Vulcano0313, Vulcano0314 and Vulcana0316) was calculated, as most values lie within the standard deviation. The elements are ordered with increasing concentration for the March average. The concentrations in the samples of October (Vulcano1013) were significantly lower than in March for the following elements: Cr, Pb, Ni, Mo, Cu, Li, B and Mg. Ba and Ca however, showed a significantly higher concentration. Although previous studies also showed seasonal variation in metal concentrations in water (Rossi and Jamet [2008], Atici et al. [2008],Atici et al. [2010] and Goswami et al. [2014]), in this work, seasonality has not been studied further.

Table 3.1 presents the averages up to 200 m depth for temperature, salinity and oxygen content obtained with the CTD during the Vulcano and Vulcana projects. The water column was divided into the mixing layer and the deep layer. The oxygen content did not change significantly over the years, but did show seasonal variability. The salinity values were used to calculate the conservative ocean concentrations of Sr, Ca, K, Mg and Na with the Marcet equation (Fig. 3.2a). The average March concentration of the reference stations showed a perfect fit for Na with the conservative ocean concentration, but a reduced concentration for Sr, Ca and Mg, while K had a higher concentration. This indicates that the conditions in the research area at the time of research could not be considered normal.

Table 3.1: Average values with standard deviation around the volcano Tagoro of the temperature, salinity and oxygen content for the Mixing Layer, Deep Layer and the entire water column up to 200 m depth, as measured using a CTD.

Cruise	Depth layer* (m)	Temperature (°C)	Salinity (-)	Oxygen (mg/L)
Vulcano0313	ML 0-58	19.91±0.27	36.89±0.02	5.10±0.02
	Deep 58-200	18.58±0.66	36.72±0.11	4.84±0.14
	0-200	19.02±0.86	36.78±0.12	4.92±0.17
Vulcano1013	ML 0-50	23.06±0.31	36.97±0.02	4.71±0.03
	Deep 50-200	19.16±1.41	36.69±0.13	4.60±0.16
	0-200	20.22±2.12	36.76±0.16	4.63±0.15
Vulcano0314	ML 0-80	18.91±0.08	36.86±0.02	5.04±0.02
	Deep 80-200	18.06±0.43	36.68±0.09	4.79±0.13
	0-200	18.42±0.55	36.75±0.12	4.90±0.17
Vulcana0316	ML 0-80	19.70±0.11	36.86±0.01	5.14±0.02
	Deep 80-200	18.69±0.63	36.71±0.10	4.98±0.11
	0-200	19.14±0.71	36.77±0.11	5.05±0.12

* Layers were defined using temperature depth profiles.

Figures 3.2b, c and d show the mean concentrations of each metal element in the seawater column up to 200 m depth at all stations around the volcano (Stations in the subgrid figures 2.2b, 2.3b, 2.4b). Also the reference stations are plotted, which showed significant anomalies in the concentrations around the volcano as presented in table 3.2. Cruise Vulcano0314 shows the largest anomalies for most elements and metal concentrations seem to have decreased over the years following the eruption, suggesting that the volcano is emitting less metals. The elements are ordered with increasing concentration for the March average of the reference stations. For the cruises Vulcano0314 and Vulcana0316 the volcano Tagoro emitted relatively more Mn, Cr, Pb and Ba (Ba only for Vulcana0316) into the ocean than other elements, as the order of increasing concentration of the elements is different around the volcano than at the reference stations.

Generally the closer the rosette got to the hydrothermal vents of the submarine volcano, the higher the metal concentration in the sampled seawater. This means that the anomalies could be higher at some stations and cruises, only because the samples were taken closer to the source and not because more metals were emitted and thus the average metal concentration of the first 200 m water column above the volcano was used.

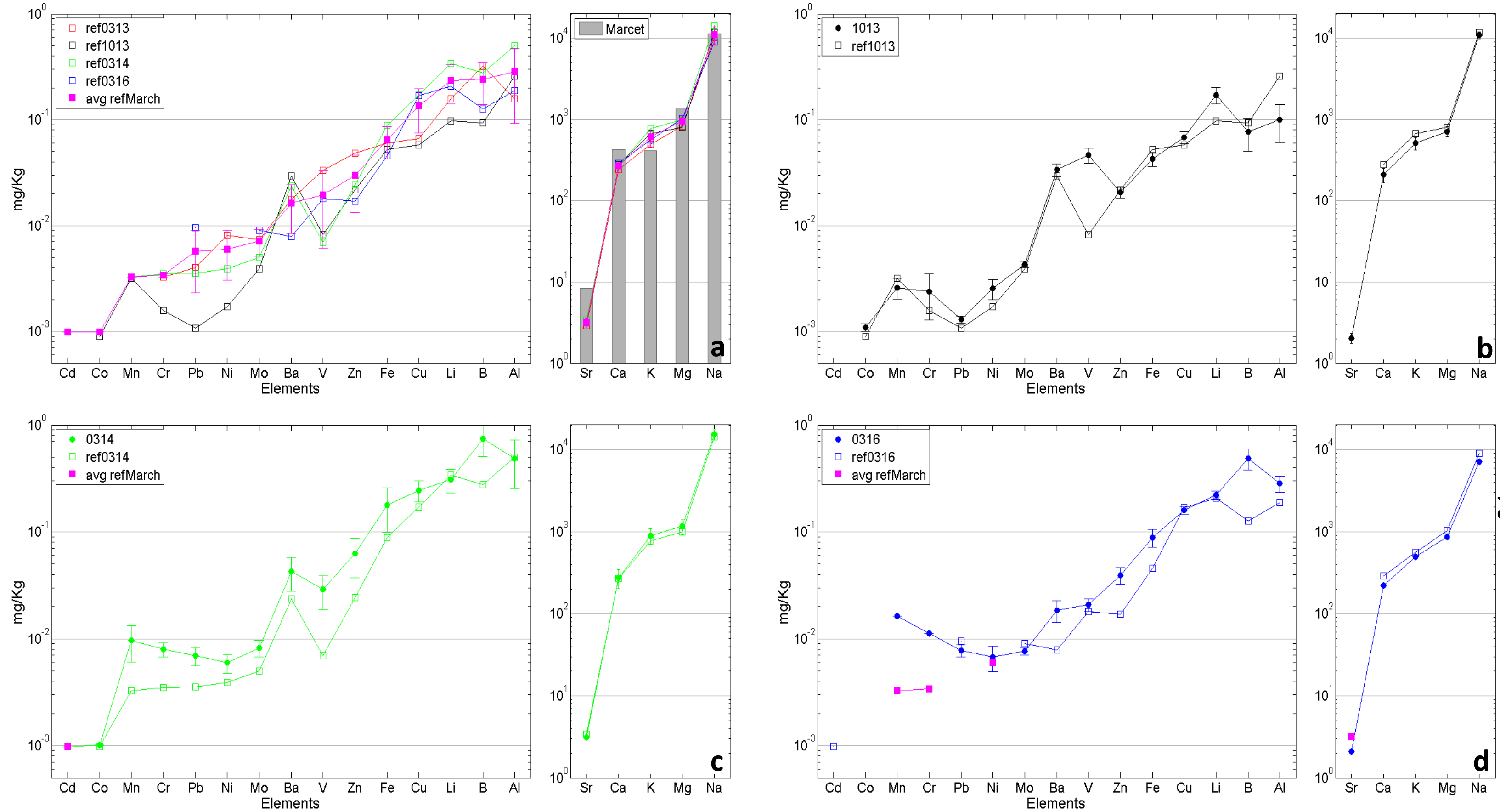


Figure 3.2: a) The mean concentrations of each metal element in the seawater column up to 200 m depth at all reference stations that are shown in figures 2.1a, 2.2a, 2.3a and 2.4a. Conservative ocean concentrations calculated with the Marcet equation are presented on the right. b)c)d) The mean concentrations with the standard deviations of each metal element in the seawater column up to 200 m depth at all stations around the volcano Tagoro and the corresponding reference stations for cruise Vulcano1013, Vulcano0314 and Vulcana0316. Locations of all stations are presented in figures 2.2, 2.3 and 2.4.

Table 3.2: Significantly different metal concentrations in the seawater around the volcano Tagoro compared to the reference stations. Values were considered significantly different when the metal concentrations at the reference station plotted outside of the standard deviation of the metal concentrations around the volcano Tagoro (Fig. 3.2).

	Vulcano1013	Vulcano0314	Vulcana0316
Element	Higher(↑)/Lower(↓)	Higher(↑)/Lower(↓)	Higher(↑)/Lower(↓)
Cd	-	-	-
Co	↑	-	-
Mn	-	↑	↑
Cr	-	↑	↑
Pb	↑	↑	↓
Ni	↑	↑	-
Mo	↑	↑	↓
Ba	-	↑	↑
V	↑	↑	↑
Zn	-	↑	↑
Fe	↓	↑	↑
Cu	↑	↑	-
Li	↑	-	-
B	-	↑	↑
Al	↓	-	↑
Sr	-	↓	-
Ca	↓	-	↓
K	↓	-	↓
Mg	-	-	↓
Na	-	-	↓

3.2 Plankton

Appendix B presents the results of the plankton analysis in tables B.1, B.2 and B.3 for cruises Vulcano0313, Vulcano1013 and Vulcana0316, respectively. Also the biomass of the plankton is presented in these tables.

3.2.1 Plankton biomass

Figure 3.3 presents the dry weight of the plankton per m^2 of seawater around the volcano (Stations in the subgrid figures 2.5b,2.6b and 2.7b) compared to the average of the reference stations and the average of the dry weight obtained by Hernández-León and Rodal [1987] in 1985. Cruises Vulcano0313 and Vulcano1013 are combined in one annual average (2013), as the weights were very similar. For cruise Vulcano0313 reference stations 26-34 were used in order to avoid possible contamination, as the wind was coming from the West during the period of the cruise (Fig. 1.4). The same was done for cruise Vulcano1013, where stations 8-10 and 13-15 were used as reference stations, as the wind was coming from the North during this period (Fig. 1.5). The mean dry weight of the reference stations increased from 798 mg/m^2 in 2013 to 4962 mg/m^2 in 2016. In 2013 the biomass was in the lower regions of the biomass levels found in 1985, when looking at the standard deviation, but significantly smaller than the biomass concentrations obtained in 2016. Around the volcano the biomass shows large variations in 2016, while in 2013 it remained very constant with the exception of station 59, the station closest the the coast. A least squares regression analysis was performed for the biomass around the volcano, showing an increase in biomass concentration towards the coast of the island El Hierro in the North with 25 and 168 mg/m^2 per 100 m for 2013 and 2016, respectively.

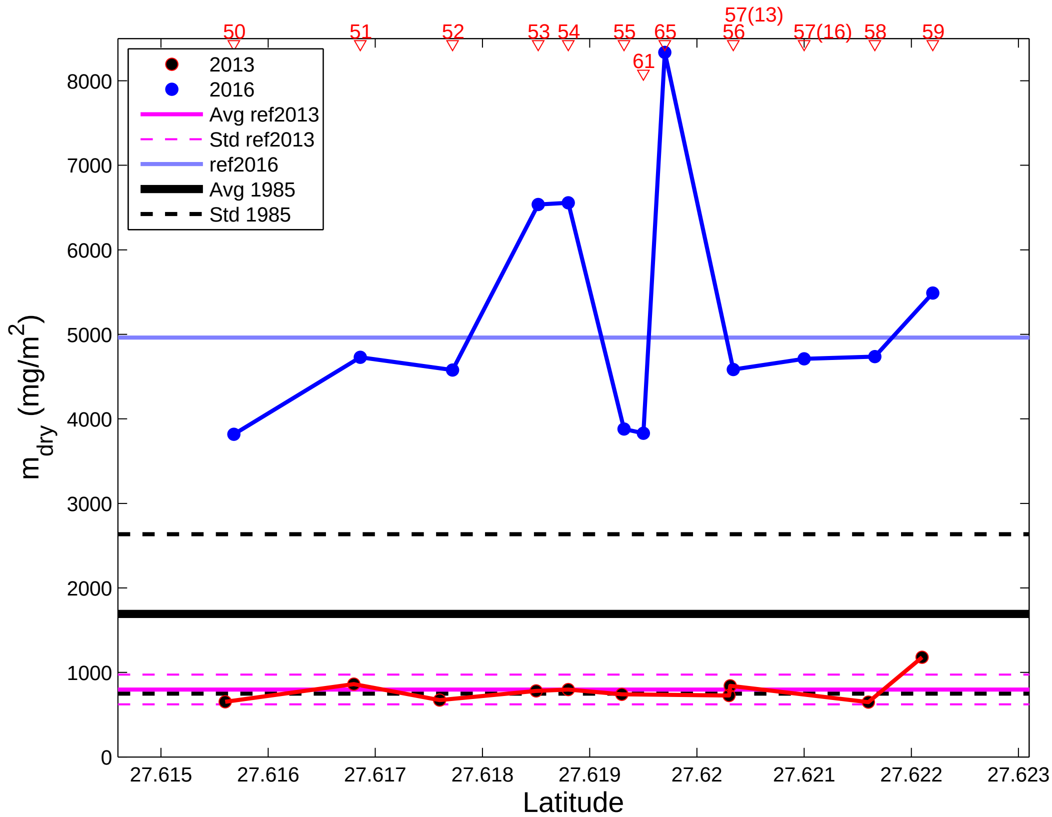


Figure 3.3: The dry weights in mg/m^2 of the plankton samples taken at the stations around the volcano Tagoro in 2013 and 2016. The station numbers are given at the top of the figure. Also the mean dry weights with standard deviations of the reference stations in 2013, 2016 and of previous research with data collected in 1985 is plotted (Hernández-León and Rodal [1987]).

The chlorophyll-a content, which is a measure for the amount of phytoplankton in the water, increased from March 2013 (Vulcano0313) to March 2014 (Vulcano0314) for both the reference stations and the stations around the volcano Tagoro. However, in March 2016 (Vulcana0316) the chlorophyll-a content decreased compared to March 2014 (Vulcano0314) as can be seen in table 3.3. which presents the chlorophyll-a content in the surface layer (5-10 m depth) of the reference stations (stations 26-34 for Vulcano0313, 8-10 13-15 for Vulcano1013, 1-6 Vulcano0314 and 1 for Vulcana0316) and stations around the volcano Tagoro (stations 50-59 for all cruises). From 2013 to 2014 the chlorophyll-a content was higher at the reference stations than around the volcano, whilst in 2016 this was the other way around, but not significantly as the value lies within the standard deviation.

Table 3.3: The chlorophyll-a content in μg/L in the surface layer (5-10 m depth) of the seawater at the reference stations and around the volcano Tagoro, as measured with a CTD.

Cruise	Reference	Volcano
Vulcano0313	0.129±0.004	0.091±0.006
Vulcano1013	0.224±0.046	0.172±0.003
Vulcano0314	0.272±0.023	0.193±0.009
Vulcana0316	0.157±0.008	0.163±0.010

The low amount of plankton biomass in 2013 and the significant increase of biomass in 2016 in the area may be due to the eruptive period. The eruption influenced the entire area as can be seen in figure 1.2 and created a highly corrosive environment, which greatly reduced the biomass of the plankton community. However the volcano also emitted and still emits large amounts of nutrients and Fe(II), which might have allowed the plankton community to recuperate and even grow in biomass over the years following the eruption (Fraile-Nuez et al. [2012], Santana-Casiano et al. [2013]). No high concentration of Fe(II) was measured in the present study, which may be because Fe(II) oxidizes quickly, but Santana-Casiano et al. [2016] did find very high values.

The biomass of the phytoplankton grew over the years following the eruption up to 2014, probably also due to the release by the volcano of these nutrients. Around the volcano the phytoplankton biomass grew less, which indicates that the conditions were less favourable than at the reference stations, but this difference was not found for the biomass of the larger (zoo)plankton. In 2016 the biomass of the phytoplankton around the volcano was very comparable to the biomass at the reference station. The overall decrease in phytoplankton biomass in 2016 could be attributed to the large increase of larger plankton, which include predatory zooplankton that prey on the phytoplankton. All this suggests that the overall plankton community is close to a new equilibrium.

3.2.2 Plankton metal content

Figure 3.4 presents the mean concentration of each metal element in the plankton samples for the reference stations and for the stations around the volcano (Fig. 2.5, 2.6, 2.7). For this figure, the same reference stations as figure 3.3 were used. The elements are ordered in the same way as the seawater samples, with increasing concentration for the March average of the seawater. The metal content in the plankton around the volcano showed many significantly different values (anomalies) compared to the plankton of the reference stations for all cruises (Table 3.4). Most of the elements showed the highest concentration in the samples from the cruises in 2013 for both the reference stations and the stations around the volcano. An example of the concentration distribution in the area during cruise Vulcano1013 for one of the anomalous metals, Fe, is given in figure 3.5, showing that the entire area around the volcano contained elevated Fe concentrations in the plankton. Reference stations 8-21 without station 19 were used, in order to create a better view of the anomaly around the volcano and an average of stations 50-58 was used for the Fe concentration in the plankton above the volcano.

The decrease of the metal concentrations in the plankton from 2013 to 2016, both around the volcano Tagoro and at the reference stations, is primarily due to the strong increase in biomass density in the area. Table 3.2, containing the anomalies in metal concentrations of the seawater, showed a decrease in the number of metals which had a significantly higher concentration in the seawater around the volcano than at the reference stations over the years. For the metal elements with the highest concentrations the anomalies in the seawater even became negative. The metal concentrations in the plankton showed this same pattern with many significantly higher concentrations found in March 2013 (Vulcano0313), a few significantly higher concentrations found in October 2013 (Vulcano1013) and only significantly lower concentrations found in March 2016 (Vulcana0316). This decrease in concentration can be attributed to the lower anomalies in the seawater and the relatively higher biomass per cubic meter above the volcano found in 2016.

The Fe concentration in the plankton was very high compared to the other metal elements around it with almost the same concentration in the seawater. This might be due to the high concentrations of Fe(II) in the seawater, that was and still is being emitted by the volcano (Santana-Casiano et al. [2013] and Santana-Casiano et al. [2016]).

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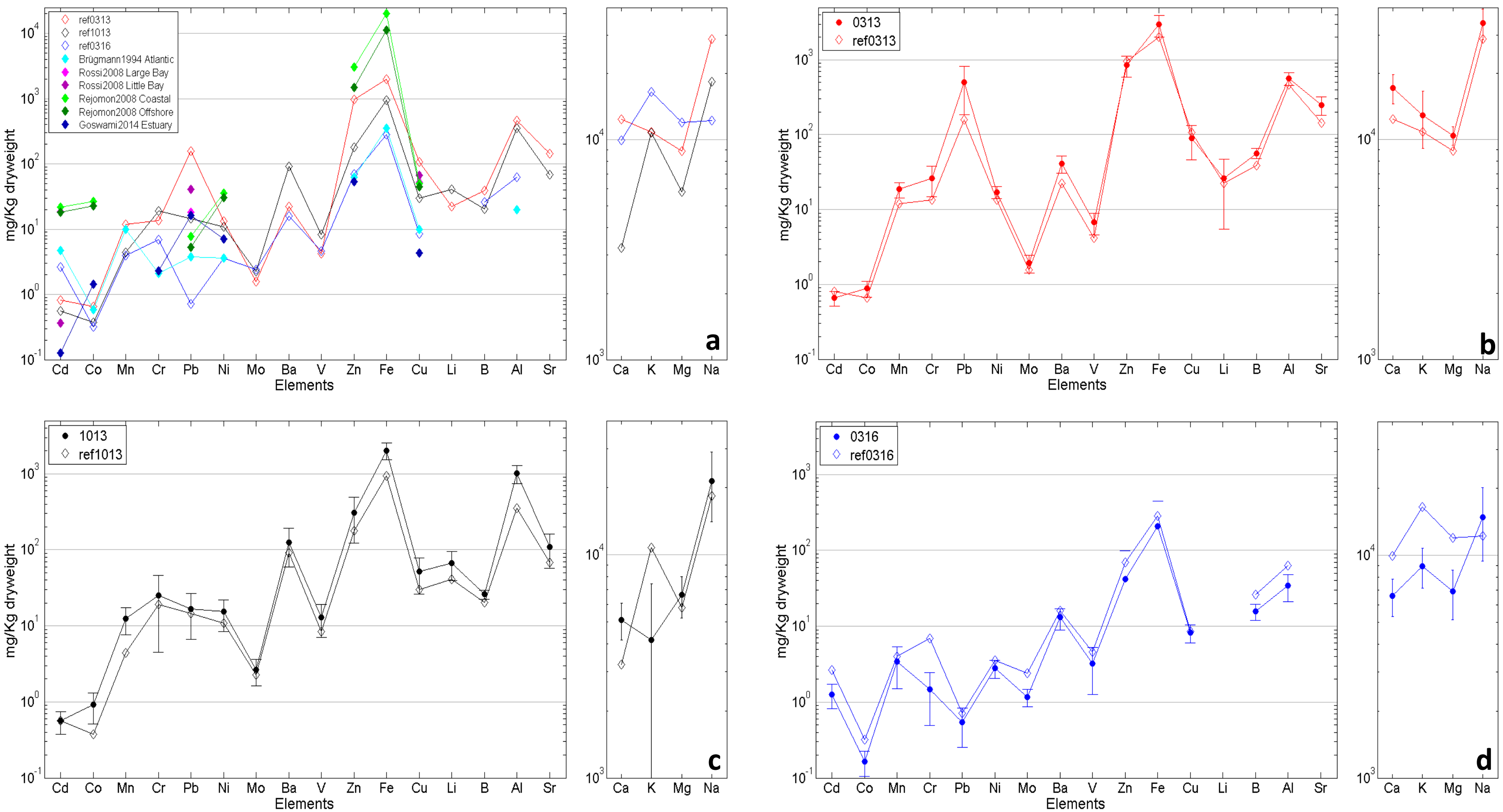

Figure 3.4: a) The mean concentrations in the plankton samples of each metal element at the reference stations that are shown in figures 2.5a, 2.6a and 2.7a. Also the concentrations of several metals in plankton obtained by previous studies are plotted here for comparison (Brügmann and Hennings [1994], Rossi and Jamet [2008], Rejomon and JOSEPH [2008] and Goswami et al. [2014]). b)c)d) The mean concentrations and standard deviations of each metal element in the plankton samples of all stations around the volcano Tagoro and the corresponding reference stations for cruise Vulcano0313, Vulcano1013 and Vulcana0316. Locations of all stations are presented in figures 2.5, 2.6 and 2.7.

Table 3.4: Significantly different metal concentrations in the plankton around the volcano Tagoro compared to the reference stations. Values were considered significantly different when the metal concentrations in the plankton at the reference station plotted outside of the standard deviation of the metal concentrations in the plankton around the volcano Tagoro (Fig. 3.4).

	Vulcano0313	Vulcano1013	Vulcana0316
Element	Higher(↑)/Lower(↓)	Higher(↑)/Lower(↓)	Higher(↑)/Lower(↓)
Cd	-	-	↓
Co	↑	↑	↓
Mn	↑	↑	-
Cr	↑	-	↓
Pb	↑	-	-
Ni	↑	-	↓
Mo	-	-	↓
Ba	↑	-	-
V	↑	-	-
Zn	-	-	-
Fe	↑	↑	-
Cu	-	-	-
Li	-	-	-
B	↑	↑	↓
Al	-	↑	↓
Sr	↑	-	-
Ca	↑	↑	↓
K	-	↓	↓
Mg	↑	-	↓
Na	-	-	-

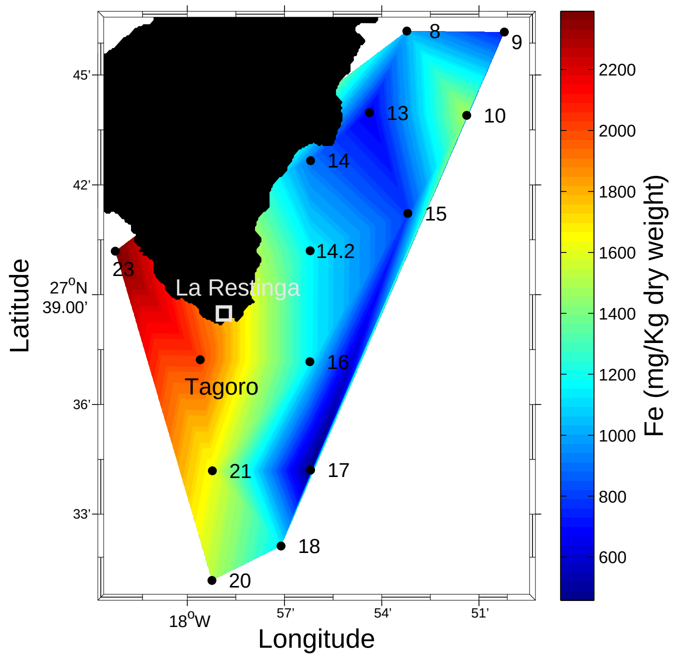

Figure 3.5: Contour map of the Fe concentration in the plankton samples from cruise Vulcano1013 obtained in the area around the volcano Tagoro and South-East of the island El Hierro, Canary Islands. The locations and numbers of the stations where the plankton samples were taken are also plotted.

Also the concentrations of several metals in plankton obtained by previous studies are plotted in figure 3.4. Brügmann and Hennings [1994] researched the accumulation of metals in plankton in the Baltic Sea and took reference samples of plankton in the North-Eastern Atlantic Ocean. The values obtained at these reference stations are not affected by volcanic activity or human contamination and are plotted in figure 3.4. The samples were also taken by towing a WP2 net with a 200 μm mesh size, but from 100 m depth to the surface (instead of 200 m in the present study). The values of the metal concentrations in the plankton found at the reference station in the present study during the Vulcana0316 monitoring cruise in 2016 were very comparable to, although slightly lower, the values found by Brügmann and Hennings [1994], except for the metals Cr and Al, which were found in higher concentrations. This indicates that in 2013 in the entire area South of the island El Hierro the plankton contained high metal concentrations (above the volcano Tagoro even higher) and that the plankton living in the area in 2016 were close to an unaffected situation concerning metal concentrations for an Atlantic Ocean plankton community, although this unaffected area is located in the North Atlantic.

Data from two studies was added to figure 3.4 to present differences in metal concentrations in plankton between polluted and unpolluted areas. Rossi and Jamet [2008] measured the concentration of several metal elements in plankton living in the Mediterranean sea. The samples were taken at two bays with a 90 μm mesh size net and showed concentrations which are similar to the concentrations found in plankton at the reference stations in 2013, but higher than 2016, except for Cd. There was a considerable environmental impact on the little bay through raw sewage and inputs from maritime traffic, while the large bay was less affected. Rejomon and JOSEPH [2008] studied the accumulation of metals in plankton in the Bay of Bengal. A 300 μm mesh size net was used to obtain the plankton samples, which contained similar and higher concentrations of metals as found at the reference stations in 2013. Anthropogenic metal contaminated rivers open into the coastal waters of the research area.

The differences in metal concentrations in the plankton between the polluted and unpolluted areas (figure 3.4a) were very similar to the differences found in the present study between the plankton living above the volcano Tagoro and at the reference stations in 2013 (figure 3.4b,c). The differences in location and in mesh size contribute to the differences in concentrations between the studies, as species of a higher trophic level were caught, which may have biomagnified the accumulated metals (Jakimska et al. [2011]). This means that the exact values of the concentrations cannot be compared between the studies.

Goswami et al. [2014] found that at certain concentrations metals affect the genes of the plankton. The highest levels of DNA damage were observed with high chlorophyll-a, in addition to higher concentrations of Cr, Cu, Ni and Pb in zooplankton during a period of low seawater pH, salinity and dissolved oxygen. Comparing the concentrations of these metals in the plankton found by Goswami et al. [2014] with the concentrations obtained in the present research (Figure 3.4) indicates that it is most likely that DNA damage has been high in the zooplankton living in the area near the volcano Tagoro.

The inability to adapt morphologically and behaviourally in order to protect themselves from predators due to high concentrations of metal in the lake, caused a large decrease in abundance of *Daphnia* zooplankton in a volcanic lake (Leoni and Garibaldi [2009]). The water contained metals in similar concentrations as found in the present research, except for Fe and Mn, which had approximately 16 and 1400 times higher concentrations, respectively. It is unclear which of the metals caused this behavioral change specifically, but this effect might also have occurred in the area of the present research.

The slightly elevated concentrations of Cd and Cr in the plankton in 2013 with their carcinogenic properties and especially the high concentration of Pb, which can damage nerve cells and the brain, may have posed a danger to human health at the end of the food chain(IARC [2012] and Chen [2013]). The larger fish presently living in the area might still contain this elevated Pb content, as it will have transferred through the chain from the contaminated plankton. Because of the strong increase in biomass, the concentration of Pb in the plankton samples of 2016 was much lower (even lower than Brügmann and Hennings [1994]), which means in the future the concentration in the fish will also decrease.

3.3 Bioconcentration factors

Figure 3.6 shows the BCFs of six metals in the plankton plotted with the corresponding metal concentrations in the seawater using logarithmic scales for cruises Vulcano1013 and Vulcana0316. Log_{10}-log_{10} least squares regressions were performed resulting in the lines shown in figure 3.6 with the slopes and coefficients of determination (R^2) displayed as well. The metals with the highest R^2s and thus the best fits were chosen for this figure. The small number of samples keep the R^2 rather low, but it shows a decline in the BCFs when the concentration of the metal in the seawater increases, resulting in the negative slopes. This negative relationship results from an ability to acclimate to elevated exposures and thereby control metal accumulation (McGeer et al. [2003]). When the slope of the regression line is greater, the plankton can acclimate better to the metal. Cu has the greatest slope in this study for both cruises (Vulcano1013 and Vulcana0316) even though it is an essential element according to Mason and Jenkins [1995] and thus needed by the organism. This could be due to the plankton using the Cu it needs after which it is very capable of regulating the accumulation of excess Cu from the seawater.

This confirms the findings of McGeer et al. [2003], who found that BCF data for Zn, Cd, Cu, Pb, Ni, and Ag were characterized by extreme variability in mean BCF values and a clear inverse relationship between BCF and aqueous exposure levels. This indicates that BCF values are inappropriate for hazard assesment.

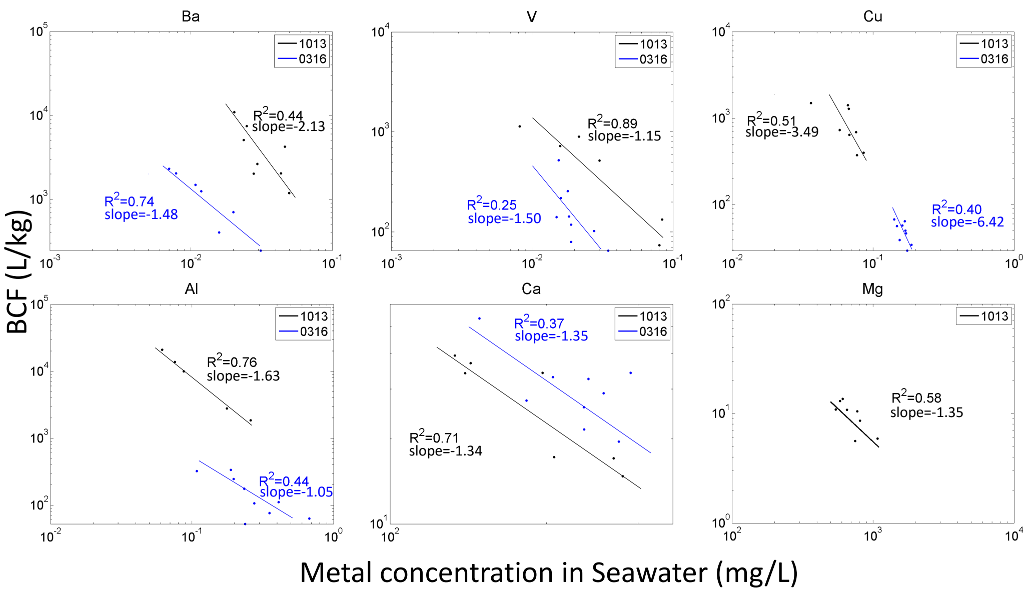

Figure 3.6: Bioconcentration factors of 6 metals for plankton living in seawater around the volcano Tagoro South of the island El Hierro, Canary Islands, during cruises Vulcano1013 and Vulcana0316. These factors are plotted against the seawater concentration and the least squares regression lines are shown with corresponding slopes and coefficients of determination (R^2).

Chapter 4

Conclusions

The present study on the submarine volcano Tagoro indicates that for this area a Rosette with Niskin bottles is an appropriate method to sample seawater for metal content analysis.

The metal concentrations in the seawater showed a seasonal variation with primarily lower concentrations in October than in March and a different order of increasing magnitude for the metal elements.

Around the volcano the metal concentrations in the seawater were significantly higher than at the reference stations, however, the amount of metals emitted seemed to be decreasing over the years (2013-2014-2016).

Relatively more of the metals Mn, Cr, Ba and Pb were emitted into the ocean by the volcano than other metals.

The metal concentrations found in the plankton living in the area of influence showed high values in 2013 compared to metal concentrations in plankton living in the Atlantic Ocean uninfluenced by volcanic or human activity, but the metal concentrations also decreased over the years (2013-2016). Around the volcano Tagoro the metal concentrations found in the plankton were, just like in the seawater, significantly higher than at the reference stations, except for 2016, which showed significantly lower concentrations. The increase in metal concentrations due to the volcano was comparable to increases in concentrations due to anthropogenic pollution.

The decrease in metal concentrations in the plankton in 2016 is primarily attributed to a large increase in biomass, especially above the volcano Tagoro. The biomass increased strongly probably due to large amounts of nutrients and Fe(II) in the seawater, which were emitted during the eruption and are still being emitted by the volcano. First the biomass of the phytoplankton grew, after which the larger zooplankton, who prey on phytoplankton, also grew strongly in biomass. The halt in biomass growth of the phytoplankton indicates that the environment is close to a new equilibrium.

The bioconcentration factors showed an inverse relationship with the metal concentrations in the seawater for each metal element, confirming the findings of McGeer et al. [2003] and indicating that BCF values are inappropriate for hazard assesment.

The high concentrations of toxic heavy metals in the plankton most likely damaged the DNA and might have affected the behaviour of the plankton. As the concentrations have decreased over the years after the eruption, especially in the plankton, there is no hazard anymore.

The plankton containing high metal concentrations in 2013 did probably transfer the metals further up the food chain, which might still be visible in the larger fish living in the area right now. But this is not a problem for the future anymore, as the metal concentrations in the plankton have decreased. This confirms that the ecosystem, after being strongly damaged and toxicated by metals from the volcano, was able to recover using the same volcano.

Chapter 5

Future research

Additional monitoring should be done as it is unknown if the biomass will continue to increase or will decrease again, as the amount of phytoplankton has already decreased. Will the biomass with this possible decrease return to the level Hernández-León and Rodal [1987] found or will, as suggested by the present study, a new higher equilibrium be found? What would this mean for the concentration of metals in the plankton?

In order to better establish whether there is any risk for human health, the metal concentrations should be quantified per step in the food chain. For example by using three different mesh sizes to separate phytoplankton from zooplankton and larger predatory species or even separating the plankton per species. By doing this it will be possible to say if an element gets magnified or diminished in the lower throphic levels, which will give an indication on how it will be further up in the chain. By analyzing the metal content in higher organisms in the area, the chain of metal transfer could be better understood.

For future research the reference stations used for the seawater sampling should be taken further away from the volcano, completely outside the potential area of influence and be combined with stations inside the area ánd stations above the volcano, so that the influence of the volcano on the entire area can be better evaluated.

Chapter 6

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Appendix A

Seawater data

Table A.1: Metal concentrations in the seawater for Vulcano0313 in mg/Kg.
** Data removed by failing the quality control.*

St	nr Niskin	Al (10^{-2})	B (10^{-2})	Ba (10^{-2})	Ca	Cd	Co	Cr (10^{-2})	Cu (10^{-2})	Fe (10^{-2})	K	Li (10^{-2})	Mg	Mn	Mo (10^{-2})	Na	Ni (10^{-2})	Pb (10^{-2})	Sr	V (10^{-2})	Zn (10^{-2})	Depth (m)
2	9	84.9*	39.4	4.10*	313	-	-	-	20.3*	10.0	823	12.1	1182	-	0.72	21427	0.72	0.46	4.55	-	8.48	201
	10	11.2	55.2	1.39	163	-	-	-	3.1	1.5	308	5.0	511	-	-	8574	-	0.40	1.85	-	2.71	151
	11	11.3	34.2	1.58	379	-	-	-	5.3	7.2	664	12.2	1158	-	0.66	22015*	-	-	4.63*	3.95	4.41	101
	12	8.9	20.9	1.38	148	-	-	-	6.5	-	344	6.4	502	-	-	8526	-	0.39	1.70	-	5.07	75
	13	11.2	13.4	1.32	162	-	-	-	3.1	1.5	307	4.9	510	-	-	8547	-	0.40	1.85	-	2.70	52
	15	77.5*	57.4	4.79*	396	-	-	0.33	6.3	23.6	676	6.2	1243	0.01*	0.80	22588	1.00	0.33	5.19	-	7.25	6
43	1	4.9	36.6	1.39	137	1.47*	1.24*	2.85*	5.0	3.2	341	7.0	498	1.38*	89.6*	13792*	0.80	0.50	3.88	2.65	2.19	1827
	2	18.3	38.1	2.70	153	0.86*	1.13*	3.40*	3.9	2.4	335	6.7	482	1.56*	98.6*	13237*	0.90	0.60	3.97	1.53	2.46	1499
	3	55.8	25.3	3.45	328	1.70*	1.25*	3.80*	25.7*	11.1	696	77.1	1141	1.50*	0.66	21573*	0.40	0.70	4.23	2.60	7.77	1201
	4	63.2	27.7	3.51	323	1.58*	1.17*	4.20*	22.7*	11.7	827	81.8	1192	1.57*	0.86	15091*	0.80	0.60	4.17	3.20	7.75	1000
	5	12.8	30.6	1.25	177	1.22*	1.22*	4.35*	14.2	2.4	371	6.9	476	1.50*	89.7*	15565*	0.46	0.72	3.82	1.91	2.37	900
	6	7.3	18.3	-	152	1.21*	1.09*	4.29*	4.0	4.0	348	7.3	484	1.64*	98.6*	13352*	1.20	0.20	3.95	1.50	3.57	798
	7	34.2	45.5	4.02	368	1.70*	1.29*	4.40*	25.0*	12.9	1061*	10.7	1302	1.53*	0.79	21773*	0.99	0.20	4.33	0.66	5.74	603
	8	32.4	70.6	3.82	223	1.70*	1.19*	3.07*	7.7	9.7	843	32.5	1161	1.48*	0.60	23437*	0.74	0.40	3.61	1.70	7.21	401
	9	23.9	17.5	4.84*	220	1.47*	1.22*	2.86*	6.9	12.7	759	30.6	1158	1.44*	0.66	24711*	4.72*	0.40	3.54	2.70	8.31	300
	10	7.2	30.6	2.74	375	1.66*	1.29*	3.10*	4.3	7.1	651	8.4	1183	1.68*	0.66	22080*	0.80	0.50	4.56	2.50	5.46	199
	11	40.8	50.6	3.39	370	1.77*	1.29*	2.80*	26.6*	10.0	1138*	12.0	1255	1.53*	0.87	23547*	0.67	0.20	4.75	1.90	7.29	150
	12	52.6	24.4	4.54*	321	1.54*	1.54*	2.70*	25.1*	10.2	1107*	12.1	1274	1.40*	0.80	23705*	0.80	0.33	4.70	3.10	8.27	100
	13	26.0	42.1	1.65	396	1.58*	1.49*	4.40*	22.6*	7.8	924*	71.1	1364	1.47*	0.79	23957*	0.66	0.50	4.74	2.80	5.27*	76
	14	76.9*	26.7	2.39	258	1.66*	1.29*	2.66*	29.7*	11.2	903*	88.9	1282	1.40*	0.80	23695*	0.80	0.40	4.13	3.50	9.33	51
	15	18.1	36.3	1.19	258	1.60*	1.20*	4.70*	16.4	4.8	691	58.1	1077	1.46*	0.60	21088*	0.90	0.60	3.75	2.90	3.44*	25
	16	13.4	49.1	1.53	330	1.49*	1.35*	3.50*	4.7	8.3	609	10.3	1050	1.39*	0.60	21037*	0.80	0.73	4.31	3.70	4.86	5
50	2	19.9	33.0	3.77	430	-	-	-	4.4	7.5	850	6.9	1319	-	0.79	23937	-	-	3.02	-	7.54	316
56	1	51.2	18.8	5.29	348	-	-	-	6.2	26.4	877	6.2	1178	-	0.73	23523	0.73	-	4.59	-	7.47	91
	3	52.0	18.5	5.34	392	-	-	-	6.4	26.1	890	6.4	1242	-	0.67	23663	0.87	-	5.81	-	7.20	73
	6	51.2	18.8	5.29	348	-	-	-	6.2	26.4	877	6.2	1178	-	0.73	23523	0.66	-	4.59	-	7.47	50
61	2	19.6	18.2	2.31	143	-	-	-	6.1	4.0	313	5.1	486	-	-	8602	-	-	1.79	-	2.77	1003
	5	4.3	20.5	1.38	150	-	-	6.99*	3.8	2.4	295	4.7	466	-	-	8328	-	-	1.67	-	2.57	600
	8	5.3	17.0	1.45	153	-	-	7.00*	3.5	2.6	301	4.9	472	-	-	8431	-	-	1.67	-	2.51	202
	10	5.4	19.5	1.58	151	-	-	6.70*	4.6	2.4	300	4.8	461	-	-	8380	-	-	1.70	-	2.48	102
	11	10.0	35.4	1.33	132	-	-	3.78*	7.2	2.1	365	7.2	478	-	-	8423	-	-	1.64	-	2.25	77
	13	5.2	19.7	1.39	150	-	-	7.03*	4.0	2.4	293	5.0	468	-	-	8446	-	-	1.67	-	2.12	25
gf61	1	5.9	13.0	1.51	176	-	-	-	2.8	2.9	393	4.3	558	-	-	10049	-	-	1.90	-	4.21	50
	2	5.4	19.7	1.73	151	-	-	7.03*	3.7	2.4	293	5.0	468	-	-	8445	-	-	1.59	-	2.26	25

Table A.2: Metal concentrations in the seawater for Vulcano1013 in mg/Kg.
** Data removed by failing the quality control.*

St	nr Niskin	Al (10^{-2})	B (10^{-2})	Ba (10^{-2})	Ca	Cd	Co (10^{-2})	Cr (10^{-2})	Cu (10^{-2})	Fe (10^{-2})	K	Li (10^{-2})	Mg	Mn (10^{-2})	Mo (10^{-2})	Na	Ni (10^{-2})	Pb (10^{-2})	Sr	V (10^{-2})	Zn (10^{-2})	Depth
13	1	-	5.43	0.84	143	-	0.05	0.04	5.21	1.52	339	13.9	473	0.27	0.32	10328	0.19	-	-	0.32	1.62	1050
	2	-	6.10	1.59	143	-	0.03	0.03	5.47	1.79	342	12.8	482	0.10	0.35	10355	0.20	-	-	0.45	1.69	801
	4	11.4	7.32	2.54	268	-	0.08	0.09	6.54	2.67	599	13.8	793	0.42	0.38	15214	0.21	-	-	0.54	1.66	601
	6	14.1	5.67	2.39	427	-	0.10	0.20	7.18	4.69	1037*	15.4	1206*	0.50	0.30	16053	0.20	-	-	0.80	1.40	299
	8	23.5	4.57	2.76	288	-	0.09	0.11	6.74	5.43	684	12.8	823	0.43	0.34	11288	0.15	-	-	0.92	2.87	201
	11	24.2	18.97	0.89	157	-	0.08	0.08	4.55	5.50	386	10.4	556	0.28	0.45	9883	0.18	-	-	0.86	1.58	100
	13	27.4	2.87	6.34	399	-	0.09	0.28	5.67	4.98	829	9.3	733	0.27	0.35	12348	0.16	0.12	-	0.67	2.98	51
	16	30.3	1.67	4.42	425	-	0.10	0.29	7.08	3.64	1189	4.6	1454	0.29	0.39	16805	0.20	0.10	-	0.79	1.47	27
	18	35.7	2.78	3.48	398	-	0.11	0.21	7.64	6.78	1030	3.9	1393	0.28	0.42	15274	0.22	0.11	-	0.62	1.89	6
50	1	12.3	0.67	6.32	328	-	0.11	0.21	7.21	4.72	981	12.3	1127	0.21	0.36	12983	0.18	-	-	1.87	1.87	335
	3	26.8	0.76	5.23	421	-	0.12	0.27	8.21	5.62	826	8.4	1272	0.35	0.39	11232	0.21	-	-	1.52	1.18	201
	4	22.6	0.89	5.04	449	-	0.10	0.20	8.10	5.14	1067	15.6	1116	0.20	0.30	15507	0.20	-	-	1.78	1.09	151
	5	15.1	6.66	5.87	143	-	0.12	0.32	6.75	7.10	391	4.2	563	0.28	0.44	9435	0.11	-	-	1.29	1.87	124
	6	23.5	0.97	4.36	433	-	0.10	0.69	5.45	4.06	1129	4.5	1416	0.30	0.40	17235	0.20	-	-	1.19	1.78	101
	7	11.5	11.56	3.17	381	-	0.10	0.20	6.73	3.46	1020	15.3	1277	0.10	0.40	16728	0.20	-	-	0.59	0.99	75
	8	14.8	16.43	2.65	449	-	0.10	0.10	7.35	7.45	1087	14.2	1225	0.20	0.29	16361	0.20	-	-	0.88	0.78	51
	9	6.3	18.25	3.83	195	-	0.08	0.05	5.47	3.39	393	4.8	542	0.50	0.35	9770	0.20	-	-	3.93	1.64	26
	10	2.2	19.82	7.28	330	-	0.09	0.21	3.87	3.29	598	4.2	819	0.32	0.31	12983	0.21	-	-	3.34	1.77	17
	11	35.0	1.67	9.06	462	-	0.10	0.30	4.93	4.24	1143	4.2	1429	0.30	0.39	17733	0.20	-	-	0.49	1.67	6
51	1	3.9	6.31	2.63	167	-	-	0.05	4.22	3.13	311	5.7	498	0.15	0.40	10288	0.20	-	2.28	3.18	2.29	246
	2	3.0	9.80	2.91	163	-	-	0.09	4.11	3.21	387	4.5	564	0.13	0.41	10921	0.22	-	1.93	4.92	2.11	202
	3	2.0	7.24	2.09	158	-	-	0.11	8.25	5.26	411	34.9	560	0.28	0.45	11293	0.38	-	2.01	3.98	2.33	150
	4	1.7	12.43	1.88	161	-	-	0.99*	9.54	6.33	413	22.5	619	0.30	0.49	9360	0.40	-	1.91	4.01	1.48	125
	5	7.8	27.18	2.83	298	-	-	0.39	7.89	5.62	429	29.9	612	0.27	0.45	9940	0.38	-	2.31	0.39	1.93	101
	6	9.2	12.98	2.91	361	-	-	0.29	8.86	4.25	539	18.5	621	0.49	3.10*	8932	0.31	-	1.73	0.12	9.37*	76
	7	17.8	17.64	2.24	398	-	0.11	0.18	7.99	5.77	627	12.2	1129	0.42	0.28	15424	0.22	-	1.83	0.23	8.36*	51
	8	14.1	28.91	2.39	427	-	0.10	0.20	7.18	4.69	1037	15.4	1206	0.50	0.30	16053	0.20	-	2.20	0.80	1.40	26
	9	11.8	28.71	2.93	387	-	0.12	0.22	5.52	3.29	912	10.5	1193	0.42	0.45	15633	0.21	0.11	2.30	0.79	7.23*	16
	10	12.3	39.03	3.35	135	-	0.10	0.25	4.98	2.81	477	4.0	643	0.20	0.49	10602	0.20	0.15	1.99	0.87	8.14*	6
52	1	0.7	3.25	1.53	97	-	0.10	0.49	7.59	5.28	465	28.0	638	0.54	0.49	9965	0.44	-	2.13	1.29	1.33	202
	2	12.9	5.23	1.21	102	-	0.15	0.32	6.23	6.72	788	22.3	673	0.48	0.23	11023	0.38	-	2.88	3.29	2.87	151
	3	9.3	7.82	2.89	398	-	0.13	0.49	7.82	5.23	875	29.9	899	0.38	0.37	13244	0.28	-	2.09	2.19	1.28	126
	4	11.2	5.23	1.87	309	-	0.10	0.69	8.09	6.22	1085	14.8	1332	0.30	0.39	16279	0.20	-	2.12	3.98	1.68	102
	5	1.1	8.83	3.64	170	-	0.12	0.03	5.78	2.54	380	10.1	589	0.10	0.45	9547	0.15	-	1.98	3.58	2.14	76
	6	2.9	9.38	2.23	198	-	0.11	0.09	6.27	3.28	409	21.0	673	0.28	0.47	9782	0.98*	-	1.87	3.81	2.98	50
	7	2.4	11.52	3.92	189	-	0.12	0.11	5.93	5.21	442	11.3	783	0.38	0.42	9283	0.58	-	1.23	2.19	2.18	25
	8	3.5	11.74	2.60	104	-	0.10	0.10	6.19	3.29	430	17.9	558	0.34	0.44	9763	0.20	-	1.30	2.98	2.21	16
	9	3.4	11.28	3.22	187	-	0.11	0.32	6.21	4.25	563	12.9	673	0.33	0.48	9924	0.27	-	1.53	3.92	2.19	4
53	1	7.8	17.66	2.98	198	-	0.12	0.15	2.98	3.92	455	4.0	650	0.19	0.50	11120	0.15	-	-	-	2.89	197
	2	8.9	15.59	1.77	213	-	0.11	0.17	3.82	2.89	487	3.6	666	0.21	0.48	11982	0.22	-	-	-	2.28	150
	9	8.8	14.98	2.06	202	-	0.10	0.18	3.58	3.18	427	3.9	635	0.20	0.49	10109	0.20	-	-	-	2.21	6
54	1	-	2.31	2.55	123	-	-	-	7.28	2.09	399	23.2	605	0.22	0.55	9030	0	-	-	-	2.91	163
	2	-	2.14	2.68	131	-	-	-	8.58	2.93	391	20.7	609	0.23	0.50	9452	0	-	-	-	2.28	126
	8	-	2.98	2.98	139	-	-	-	8.99	3.91	397	22.0	613	0.18	0.49	9448	0	-	-	-	2.98	6
55	1	-	1.23	5.02	134	-	-	-	7.82	4.83	355	22.7	544	0.17	0.53	9339	0	-	0.003*	7.38	2.57	130
	2	-	2.77	4.78	130	-	-	-	8.25	4.12	307	21.0	599	0.22	0.45	9249	0	-	0.002*	8.36	2.18	101
	3	-	3.67	5.26	177	-	-	-	2.24	4.02	323	28.8	588	0.11	0.48	2310*	0	-	0.004*	8.02	2.01	76
56	1	-	1.89	4.34	150	-	-	-	8.47	4.09	346	22.9	566	0.28	0.40	9300	0	-	0.003*	8.42	1.84	91
	3	-	1.33	3.98	133	-	-	-	7.26	4.02	388	21.8	538	0.33	0.38	9329	0	-	0.004*	8.26	1.76	75
	7	-	1.78	4.78	145	-	-	-	8.02	4.41	343	21.0	549	0.21	0.39	9331	0	-	0.001*	8.56	1.97	5

Table A.3: Metal concentrations in the seawater for Vulcano0314 in mg/Kg.

** Data removed by failing the quality control.*

St	nr Niskin	Al (10^{-2})	B (10^{-2})	Ba (10^{-2})	Ca	Cd (10^{-2})	Co (10^{-2})	Cr (10^{-2})	Cu (10^{-2})	Fe (10^{-2})	K	Li (10^{-2})	Mg	Mn (10^{-2})	Mo (10^{-2})	Na	Ni (10^{-2})	Pb (10^{-2})	Sr	V (10^{-2})	Zn (10^{-2})	Depth (m)
13	1	62.8	18.6	8.60	340	-	-	-	30.4	67.6	1486	55.6	2060	2.00*	1.40*	19160*	1.20*	1.00*	-	3.20	3.40	1044
	4	44.2	34.4	4.80	436	-	-	-	24.4	17.6	1508	53.8	2100	1.80*	1.40*	20600*	-	0.60	-	9.60*	5.40	701
	6	20.6	55.0	5.40	494	-	-	-	55.6*	14.6	1928*	67.8*	2320*	1.80*	1.40*	19800*	0.60	0.60	-	12.0*	3.20	500
	8	60.0*	181.6*	1.20	264	-	-	-	17.4	12.0	682	17.0	1008	-	0.80	16640	-	0.80	3.52	-	5.20	250
	11	17.7	24.8	2.28	248	-	0.10	0.36	10.5	5.7	623	24.3	867	0.30	0.49	12965	0.40	-	3.22	-	1.68	126
	15	110.3	15.7	2.91	313	-	0.10	0.35	26.8	11.0	1067	55.7	1224	0.35	0.35	15180	0.35	0.05	-	0.46	1.62	26
	17	88.4	108.2	2.40	276	-	-	-	23.0	20.0	686	37.6	978	-	0.80	16460	-	0.80	3.78	-	8.20	5
50	1	90.2	86.2	2.20	226	-	-	-	19.8	23.6	600	38.2	770	-	0.80	15680	-	1.00*	3.44	-	12.00	344
	2	76.8	134.4	22.0*	218	-	-	-	21.0	27.8	602	41.0	806	-	0.80	15580	-	0.60	3.40	-	10.60	251
	6	102.9	7.6	2.86	322	-	0.10	0.35	21.6	10.8	1029	47.7	1308	0.20	0.36	14705	0.20	0.15	-	0.86	1.57	101
	9	66.2	128.6	2.20	238	-	-	-	17.8	19.6	634	32.6	878	-	0.80	15820	-	0.80	3.52	-	10.40	52
	12	99.6	93.2	2.60	174	-	-	-	27.8	25.6	678	45.0	902	-	0.80	16040	-	0.80	3.24	1.40	11.20	5
51	5	35.1	43.7	3.31	277	0.10	0.10	0.97	68.9*	6.8	833	-	1063	0.39	0.68	11016	0.58	0.49	-	-	2.92	101
52	1	32.4*	71.2*	3.45*	242*	-	0.10*	1.78*	52.6*	7.8*	784*	-	1036*	0.30*	0.69*	11049*	0.99*	0.10*	-	-	2.07*	205
	7	37.8*	48.8*	6.40*	416*	-	-	-	51.8*	25.8*	1558*	81.4*	2140*	1.80*	1.40*	22400*	-	0.60*	-	1.00*	4.00*	50
	9	75.4*	10.4*	4.60*	424*	-	-	-	28.8*	66.4*	1444*	49.4*	2100*	1.80*	1.40*	19640*	1.00*	0.80*	-	-	2.60*	5
53	1	37.2	73.6	1.40	108	-	-	-	20.8	17.6	622	30.8	762	-	0.80	15080	-	0.60	2.84	-	12.20	185
	3	51.6	158.2	2.80	302	-	-	-	21.8	13.2	618	35.6	1082	-	0.80	23000	-	0.80	3.62	8.80	11.60	125
	5	15.8	80.4	1.20	73	-	-	-	20.0	20.4	652	23.4	826	-	0.80	15360	-	0.40	2.20	-	15.60	76
	9	42.2	65.6	2.40	176	-	-	-	24.2	21.4	688	30.8	894	-	0.80	15860	-	0.80	3.30	-	14.20	51
	11	12.4	32.2	1.58	254	-	0.10	0.69	10.3	5.4	724	23.8	936	0.20	0.59	12181	0.40	0.10	-	-	1.49	2
54	1	7.2	30.0	4.83	245	-	0.10	0.27	9.7	3.5	745	26.9	1025	0.20	0.59	11632	0.36	0.00	-	-	1.28	168
	2	27.6	40.6	8.80	612	-	-	-	55.2	16.4	1762	68.8	2160	1.80	1.40	20200	0.60	0.80	-	8.60	4.20	124
	3	40.8	86.4	2.40	188	-	-	-	25.4	25.2	666	26.8	1010	-	0.80	21600	1.2*	0.60	3.08	9.00	14.00	100
	6	39.6	93.6	1.60	138	-	-	-	22.6	15.4	638	33.8	986	-	0.80	21800	0.60	0.80	2.76	1.60	13.20	49
55	1	120.8	27.2	15.40	570	-	-	-	20.4	69.8	1562	12.2	2120	2.00	1.40	20000	1.00	1.40	-	6.00	5.20	133
	3	9.4	86.0	-	208	-	-	-	14.2	16.6	634	16.6	764	1.60	0.80	21200	-	0.80	3.26	7.20	15.40	73
	4	13.9	53.4	2.84	201	-	0.10	1.08	17.4	3.3	764	48.3	999	0.10	0.69	10580	0.29	0	-	0.39	1.27	50
	5	7.4	91.8	1.00	132	-	-	-	17.4	11.6	698	22.2	942	-	0.80	11200	-	0.60	3.02	3.20	14.40*	25
	6	55.4	63.1	9.00	260	-	0.10	1.56*	28.4	9.8	878	13.2	1017	0.49	0.68	10563	0.59	0.20	-	-	2.84	5
56	2	338.8	97.8	8.25	355	0.10	0.13	2.90	71.3	87.5	818	-	992	4.32	0.79	10606	2.75	1.08	-	-	4.32	74
	7	19.2	50.2	5.40	530	-	-	-	50.0	18.0	1808	66.4	2260	1.60	1.40	19920	-	0.80	-	6.00	4.00	24
	8	17.3	31.8	2.06	270	-	0.10	0.29	12.0	6.1	612	21.1	933	0.29	0.59	13332	0.39	0	-	-	1.96	5
58	1	9.6	97.8	-	161	-	-	-	14.6	13.0	676	15.8	704	-	0.80	20200*	-	0.80	3.20	9.20*	13.6*	184
	4	13.0	97.0	3.00	250	-	-	-	25.4	13.8	792	29.0	1246	-	0.80	22400*	-	0.60	3.40	10.8*	14.2*	101
	8	48.0	47.4	9.00	520	-	-	-	24.8	22.8	1918	14.0	1822	2.20	1.20	20800*	-	1.20*	-	4.80*	4.60*	61
	9	15.2	112.0	3.00	185	-	-	-	24.4	11.6	842	24.2	1232	-	1.00	21600*	-	0.60	2.98	18.4*	12.0*	25
	10	10.0	105.0	1.80	126	-	-	-	25.2	11.6	942	34.0	1272	-	0.80	22400*	-	0.40	2.60	15.2*	13.0*	5
59	1	19.6	94.1	2.77	294	-	0.10	0.79	14.6	5.6	750	28.9	1038	0.30	0.69	11373	0.49	0	-	2.18	1.48	166
	3	36.2	146.0	2.40	208	-	-	-	24.2	14.0	754	30.4	1106	-	1.00	20800*	-	0.80	3.28	11.4*	10.40*	124
	6	14.8	134.4	2.80	218	-	-	-	23.0	11.8	764	23.4	1144	-	1.00	21200*	-	0.80	3.20	11.6*	10.40*	51
	7	10.2	86.6	-	83	-	-	-	19.4	14.2	672	26.2	834	-	0.60	15560	-	0.60	2.26	-	19.2*	25
	8	29.6	88.6	1.60	117	-	-	-	20.4	17.4	662	28.8	846	-	0.80	15400	-	0.60	2.82	-	15.4*	5
61	1	12.6	19.0	4.26	150	-	0.10	0.30	10.6	8.7	405	31.2	776	0.50	0.59	10897	0.40	-	2.15	0.40	1.88	120
	2	38.0	58.0	6.80	370	-	-	-	21.4	24.0	1484	43.6	2080	3.40	1.40	21000	-	0.60	-	9.20	5.20	113
	3	86.0	191.8	6.80	248	-	-	-	15.0	24.2	866	8.0	980	1.80	0.80	16940	-	1.20	3.66	-	5.20	102
	4	36.2	46.3	8.15	290	-	0.10	0.88	6.1	6.3	718	6.5	907	0.59	0.59	12758	0.39	0.29	-	1.18	2.36	89
	7	11.1	17.1	1.29	157	-	0.10	0.25	8.1	3.8	546	27.2	668	0.20	0.40	12287	0.40	-	2.63	-	2.38	26

Table A.4: Metal concentrations in the seawater for Vulcana0316 in mg/Kg.

** Data removed by failing the quality control.*

St	**nr** Niskin	**Al** (10^{-2})	**B** (10^{-2})	**Ba** (10^{-2})	**Ca**	**Cd** (10^{-2})	**Co**	**Cr** (10^{-2})	**Cu** (10^{-2})	**Fe** (10^{-2})	**K**	**Li** (10^{-2})	**Mg**	**Mn** (10^{-2})	**Mo** (10^{-2})	**Na**	**Ni** (10^{-2})	**Pb** (10^{-2})	**Sr**	**V** (10^{-2})	**Zn** (10^{-2})	**Depth**
1	1	26.3	21.8	0.79	252	-	-	-	19.0	5.7	549	22.0	852	-	0.89	9394	-	1.09	-	-	3.55	1198
	3	69.8	127.4	1.78	274	-	-	-	20.9	10.6	547	29.0	971	-	0.79	9837	-	1.09	-	2.96	2.37	1000
	5	36.9	11.8	0.89	239	-	-	-	18.4	6.5	551	25.0	838	-	0.79	9294	-	0.89	-	0.99	1.87	797
	7	12.3	32.0	0.59	252	-	-	-	15.2	3.6	556	19.8	922	-	0.79	9625	-	0.99	-	0.99	1.68	497
	8	34.1	13.6	0.79	225	-	-	-	17.4	5.7	554	23.7	828	-	0.89	9309	-	0.79	-	1.08	1.87	251
	9	18.6	10.5	0.69	275	-	-	-	14.6	4.9	567	18.3	939	-	0.89	9612	-	0.89	-	2.27*	1.48	201
	10	5.5	13.6	0.69	318	-	-	-	18.7	3.2	607	24.5	1154	-	0.89	8805	-	0.89	-	2.76*	1.58	151
	11	20.5	124.9*	0.69	317	-	-	-	16.4	4.6	556	19.0	1062	-	0.89	8763	-	0.98	-	3.34*	1.38	103
	13	7.5	8.7	0.79	272	-	-	-	16.4	2.6	552	19.1	999	-	0.99	8817	-	0.99	-	3.46*	1.29	50
	15	67.3	23.6	1.28	228	0.10	-	-	18.0	11.1	523	23.4	883	-	0.79	9745	-	1.08	-	2.26	3.73	6
50	1	92.8	21.7	1.77	176	-	-	-	20.0	11.5	458	23.9	672	-	0.69	9628	0.39	1.08	2.75	1.18	4.63	350
	2	82.2	41.6	11.01*	305	-	-	-	21.0	14.1	556	24.8	1042	-	0.89	10031	-	0.79	-	2.36	1.48	252
	6	56.3	29.8	10.12*	250	-	-	-	17.8	7.4	525	21.2	824	-	0.88	9372	-	0.79	-	-	2.06	101
	8	78.0	26.3	8.96*	243	-	-	-	19.1	10.6	547	25.1	848	-	0.79	9392	-	0.79	-	-	1.28	50
	10	70.9	25.5	6.31*	251	-	-	-	18.1	9.7	551	25.2	874	-	0.89	9378	-	0.79	-	1.48	1.08	7
52	1	53.9	44.8	2.17	311	-	-	-	19.8	12.6	539	25.5	1094	-	0.89	8813	-	0.99	-	2.56	2.76	219
	6	37.3	35.1	0.69	177	-	-	-	14.0	5.4	501	20.5	753	-	0.79	9300	-	0.59	-	0.89	2.17	49
	8	17.7	23.8	0.49	291	-	-	-	15.4	3.0	547	21.0	998	-	0.89	8850	-	0.99	-	2.07	0.99	5
53	1	40.2	28.1	0.89	250	-	-	-	15.0	5.9	518	18.2	861	-	0.79	9634	-	0.69	-	0.59	1.38	212
	3	33.8	38.0	0.89	308	-	-	-	18.7	6.4	564	21.4	1114	-	0.89	8844	-	0.89	-	2.37	2.17	123
	5	47.0	16.5	0.89	261	-	-	-	17.8	6.3	554	25.1	916	-	0.89	9390	-	0.98	-	1.48	1.57	75
	6	32.7	15.8	0.59	234	-	-	-	15.3	6.6	534	20.6	829	-	0.88	9094	-	0.88	-	0.59	2.46	50
	8	17.9	32.8	0.69	307	-	-	-	17.5	3.6	554	20.1	1071	-	0.88	8684	-	1.08	-	2.06	1.96	5
54	1	9.5	129.5	0.75	233	-	-	1.39	15.9	5.7	525	29.5	865	-	0.64	4228	0.32	0.54	-	-	1.82	183
	3	35.2	25.4	0.59	279	-	-	-	14.5	9.5	556	21.0	944	-	0.88	9626	0.29	1.08	-	2.16	2.26	126
	4	42.2	104.5	2.56	271	-	-	-	22.2	8.0	527	37.9	911	-	0.72	4006	-	0.51	-	0.72	1.33	100
	6	14.1	82.4	2.19	182	-	-	-	18.9	3.7	482	34.2	659	-	0.60	4013	-	0.50	-	-	1.29	51
	8	10.0	97.8	1.58	218	-	-	-	14.0	2.9	483	28.5	722	-	0.59	3920	-	0.49	-	-	0.69	6
55	1	21.5	116.9	1.78	250	-	-	-	19.6	6.0	511	37.1	862	-	0.69	3745	0.30	0.40	-	-	1.58	156
	3	8.6	155.2	0.92	218	-	-	-	12.6	3.1	486	25.9	697	-	0.72	4193	-	0.51	-	-	1.03	101
	4	4.3*	28.7*	-	36*	-	-	-	16.8*	8.3*	86*	47.5*	109*	-	1.98*	3347*	0.40*	1.68*	0.36*	-	9.61*	74
	5	7.2	144.8	1.05	237	-	-	-	12.5	3.4	485	24.5	795	-	0.63	4134	-	0.52	-	-	1.26	49
	7	10.2	37.2	0.59	294	-	-	0.88	18.7	8.9	586	25.2	1012	-	0.88	9666	0.49	1.08	-	2.75	1.87	5
56	1	13.0	48.6	0.79	68	-	-	-	10.1	5.8	461	25.3	582	-	0.40	4065	0.40	0.49	1.56	-	6.13	103
	2	17.7	25.7	4.81	338	-	-	-	13.5	4.1	546	13.8	1149	-	0.98	8846	-	0.98	-	4.91	6.68	74
	3	31.1	46.4	1.09	87	-	-	-	16.5	7.1	511	29.1	876	-	0.49	4239	0.40	0.49	-	2.08	7.51	51
	5	25.3	56.7	0.88	73	-	-	-	13.7	9.9	427	17.1	605	-	0.49	4066	0.39	0.49	-	-	3.71	6
58	1	23.5	50.9	0.89	68	-	-	-	11.0	6.7	420	22.3	696	-	0.39	4185	0.39	0.49	1.51	-	3.75	184
	4	19.4	34.0	0.59	281	-	-	-	19.7	4.5	527	23.1	974	-	0.89	8890	-	0.89	-	1.97	1.68	98
	6	20.9	25.4	0.69	286	-	-	-	19.3	5.6	556	25.5	1012	-	0.88	8795	-	0.88	-	2.26	2.16	50
	8	10.9	43.7	0.69	80	-	-	-	8.8*	12.7	439	21.6	746	-	0.30*	3931	0.69	0.49	1.97	1.08	4.14	5
65	1	28.8	38.5	0.99	73	-	-	-	13.2	24.4	435	23.7	647	-	0.39	4130	0.49	0.49	1.58	-	5.72	138
	2	33.3	25.2	5.33	300	-	-	-	16.8	7.5	525	18.8	986	-	0.99	8759	0.30	1.18	-	3.06	12.23	99
	3	11.6	46.4	0.97	65	-	-	-	15.5	6.2	521	26.2	814	-	0.49	3868	0.97	0.58	1.36	0.78	4.76	73
TY01	1	16.1	12.4	3.15	272	-	-	-	17.6	6.2	485	18.2	972	-	0.88	8819	-	0.98	3.24	3.74	7.67	97
TY11	1	20.2	40.7	0.79	100	-	-	-	10.2	11.0	462	17.0	740	-	0.49	4014	0.39	0.59	1.57	0.49	3.44	127
	2	16.5	41.0	0.88	81	-	-	-	17.1	20.4	447	28.7	620	-	0.49	3920	3.80	0.59	1.60	-	10.04	126
TY12	1	20.7	18.7	2.37	259	-	-	-	14.5	8.1	378	15.9	852	-	0.89	8733	0.49	1.08	3.00	1.97	3.06	128
	3	4.6	138.3	0.69	254	-	-	1.08	9.1	180.5*	477	17.6	813	2.06	0.88	3747	0.29	0.49	-	-	0.88	122
TY37	25	45.2	25.6	4.44	255	-	-	-	17.6	16.9	506	16.2	961	1.18	0.89	10161	0.69	1.09	-	2.27	4.54	127

Appendix B

Plankton data

Table B.1: Dry weight and metal concentrations of the plankton samples of cruise Vulcano0313 in mg/Kg dry weight.
** Data removed by failing the quality control.*

St	m_{dry} (g)	Al	B	Ba	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Mo	Na	Ni	Pb	Sr	V	Zn
1	0.190	1329	68.6	87.5	22237	1.05	1.97	45.0	153.9	4632	3605	27.2	7395	38.6	1.97	13553	39.1	320	-	8.55	1421
2	0.202	848	42.0	46.5	20050	0.87	1.11	25.7	357.7	1856	1324	69.2	6720	18.6	1.24	13614	39.2	203	-	4.70	1361
3	0.209	1220	71.2	94.5	28110	0.96	1.79	80.7	175.8	4175	5897	14.4	10538	34.9	2.03	35526	37.7	350	334	11.48	1280
4	0.182	897	56.7	61.1	23077	0.69	1.10	31.2	87.0	2720	4876	21.4	8668	24.5	1.51	31593	18.5	163	-	6.18	791
5	0.268	625	51.5	51.6	15019	0.84	1.49	33.4	59.4	3535	5457	15.9	10075	23.0	1.21	24907	17.2	82	-	5.22	684
6	0.318	544	50.1	51.7	14308	0.63	1.10	24.8	84.1	2909	14623	18.3	13208	19.2	1.18	28381	21.5	92	-	5.42	534
7	0.200	871	48.9	43.8	16875	0.88	1.25	50.4	98.4	3250	10288	8.3	9088	22.1	1.38	30875	26.0	638	220	6.13	1080
8	0.244	823	39.8	40.7	15984	0.82	0.72	29.6	114.8	2346	16086	17.1	10246	16.5	1.23	32275	16.4	66	152	4.10	628
9	0.280	518	39.4	27.1	11875	0.80	0.62	15.5	39.8	2232	17589	16.4	10982	11.7	1.07	36607	13.4	54	156	5.36	469
10	0.191	661	40.8	32.2	13874	0.79	0.79	17.4	67.5	2461	4620	27.7	8455	15.4	1.18	30366	24.6	61	263	4.97	1018
11	0.249	484	38.7	24.0	11044	0.60	0.60	13.1	45.1	1637	21386	26.4	11847	8.4	0.80	33233	9.0	24	153	2.71	383
12	0.337	243	24.9	11.4	6320	0.22	0.30	15.7	298.2	529	9421	36.1	9421	5.2	0.89	32270	7.3	20	137	3.19	193
13	0.304	508	23.2	15.0	8306	0.58	0.49	11.4	65.5	1028	4054	63.2	5477	8.0	0.82	22862	8.6	118	-	2.96	345
14	0.176	1068	74.0	72.7	26420	1.28	4.69	18.8	86.1	5938	5440	43.3	10781	79.3	1.56	33097	17.9	403	-	21.31	911
15	0.242	1054	68.0	64.9	22934	0.83	3.20	22.7	53.4	4339	4876	11.6	10217	63.3	1.45	36983	15.4	343	-	14.77	693
16	0.090	503	5.3	123.3	110000*	0.28	-	-	69.2	283	1900	43.3	881	4.4	-	2222	2.5	48	744	3.89	123
17	0.250	621	33.4	17.7	12200	0.50	0.50	8.8	78.6	1220	6640	75.2	9220	9.5	0.70	32800	11.4	64	-	4.10	643
18	0.262	686	45.8	38.8	16412	0.48	0.95	34.8	126.9	1956	4447	43.0	8225	18.4	2.00	35115	19.0	213	-	5.92	964
19	0.174	751	45.1	57.6	16236	0.72	0.86	28.3	129.7	2170	13089	29.0	8606	17.8	2.30	34914	18.4	382	-	5.75	1070
20	0.313	484	57.7	48.6	17412	0.64	0.80	22.5	202.9	2292	16933	14.5	10783	15.7	2.16	28514	14.2	237	-	4.95	879
21	0.320	473	50.4	46.3	17578	1.09	0.78	24.2	189.8	2250	14375	33.0	10625	16.3	1.72	31172	15.2	327	-	4.92	1039
22	0.237	723	47.4	27.5	17511	0.53	0.63	20.6	129.7	3133	6023	50.1	8671	12.9	1.69	41983	13.0	68	274	7.07	1266
23	0.139	1014	83.3	49.5	28597	0.90	1.08	41.5	194.2	5522	6799	66.0	10971	27.2	2.70	55036	60.6	1036	300	15.65	1960
24	0.234	484	56.8	30.1	19979	0.64	0.64	24.3	81.7	3344	4615	28.4	10011	14.9	2.03	41239	14.7	1041	210	7.26	1592
25	0.235	320	46.6	15.7	13404	0.64	0.43	9.0	66.5	1979	4979	28.6	10426	9.6	0.96	38617	12.0	273	162	4.36	889
26	0.288	496	49.0	42.1	16667	0.52	0.69	11.5	85.4	1927	13368	-	11198	16.1	4.17	31771	9.8	115	-	5.03	619
27	0.189	685	52.4	21.7	16534	0.79	0.93	20.2	109.7	3333	4431	34.9	8981	18.9	1.46	37698	15.3	239	216	6.35	1062
28	0.276	486	45.7	19.3	15036	1.00	1.00	10.2	83.3	2826	4004	24.5	9601	17.5	1.09	34239	18.2	225	242	4.44	884
29	0.280	232	26.8	8.8	8536	0.89	0.45	5.7	49.0	1304	2411	20.1	6580	5.7	0.80	17946	10.4	120	88	2.59	1509
30	0.242	181	28.9	10.6	8450	0.83	0.41	9.4	62.8	1271	11157	14.8	7696	7.0	0.52	22211	12.1	52	95	4.13	650
31	0.144	1196	58.9	33.9	20312	1.39	0.69	20.7	70.0	1410	22049	22.0	12986	13.2	1.56	42187	20.0	273	186	3.82	1219
32	0.210	448	24.6	27.0	8643	0.48	0.48	12.5	57.1	1333	14405	14.5	7107	7.7	0.83	24286	7.6	169	77	3.45	704
33	0.232	246	31.5	32.1	10754	0.65	0.65	15.2	70.0	2241	14871	13.8	9752	10.2	3.13	26293	15.5	81	182	4.09	1304
34	0.167	195	33.4	6.9	6991	0.75	0.60	15.9	374.3	2335	10853	33.4	6302	10.8	0.45	21856	11.1	157	65	3.74	735
50	0.211	639	46.8	29.6	14218	0.59	0.83	26.5	56.6	2299	10640	17.1	8519	17.3	2.96	32820	15.8	226	220	5.09	932
51	0.286	522	50.8	38.6	17133	0.79	1.14	20.5	61.6	3462	11364	14.9	10752	18.4	1.66	27885	15.6	264	-	5.86	771
52	0.226	551	46.5	22.6	15155	0.55	0.77	56.5	55.4	2069	6582	44.5	9082	15.7	1.44	32522	13.8	376	168	5.31	662
53	0.278	434	56.5	31.5	14029	0.81	0.81	14.7	39.2	2608	17086	29.4	10162	14.3	1.26	28417	13.5	279	-	5.04	658
54	0.276	476	53.7	49.4	17663	0.63	0.91	22.9	102.4	3487	16757	12.1	11866	16.9	1.72	30344	16.0	299	-	6.97	933
55	0.230	530	49.2	49.9	16522	0.54	0.65	19.6	172.8	2022	14022	19.3	10391	14.8	1.74	39674	14.5	214	298	5.87	725
56	0.255	668	61.8	43.7	15980	0.49	0.78	25.4	86.6	2529	18725	77.7	11373	16.0	2.16	32745	19.7	683	-	5.78	683
57	0.198	481	60.9	43.8	20202	0.51	0.63	25.6	66.3	2361	10619	21.7	11364	20.1	2.40	42677	20.6	1105	-	6.06	741
58	0.203	798	72.7	57.5	22167	0.86	1.11	30.0	145.3	4963	11897	14.0	10517	26.4	2.22	41256	22.4	890	313	11.33	1539
59	0.277	548	67.1	45.0	18682	0.81	1.26	20.1	105.6	3782	11011	11.0	10469	25.9	1.71	31047	19.0	690	-	10.29	819
61	0.261	248	38.9	19.0	12261	0.67	0.38	8.0	51.8	1724	12739	13.0	8400	9.3	0.96	28161	10.8	196	152	4.89	927

Table B.2: Dry weight and metal concentrations of the plankton samples of cruise Vulcano1013 in mg/Kg dry weight.

St	m_{dry} (g)	Al	B	Ba	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Mo	Na	Ni	Pb	Sr	V	Zn
8	0.141	252	25.5	57.8	3138	0.89	-	6.0	14.2	1032	15745	45.4	7908	4.26	1.77	25532	6.7	4.4	61.2	8.7	91
9	0.182	375	13.5	102.7	2871	0.27	-	14.8	20.7	742	5467	21.2	3571	2.88	4.12	14560	3.6	2.7	76.5	8.5	35
10	0.189	426	21.8	216.9	3638	0.40	0.40	39.2	33.1	1508	10013	32.9	6310	5.69	2.51	17593	14.9	4.8	66.0	8.9	197
13	0.108	271	7.2	28.2	1206	-	-	5.3	7.2	667	2824	20.1	2042	2.08	2.08	6852	1.2	1.9	37.7	5.6	19
14	0.152	400	23.5	87.3	4063	0.66	0.33	6.7	28.9	906	12516	74.2	7089	5.76	1.48	21217	8.4	9.2	77.1	7.9	479
14b	0.136	392	25.6	43.9	2518	0.55	-	4.8	18.4	1165	13897	66.4	6820	5.33	2.94	22610	3.3	3.3	50.2	9.0	35
15	0.127	382	29.5	55.1	4429	0.59	0.39	41.7	76.6	801	18287	52.4	7992	5.91	1.57	24213	30.1	64.0	91.1	10.6	252
16	0.116	491	27.2	66.2	4397	0.65	-	9.1	39.4	1164	17651	92.7	8793	6.25	1.72	27371	10.8	41.4	78.2	7.8	349
17	0.33	315	28.6	19.5	5424	0.53	0.23	3.3	29.9	457	8333	-	14091	2.73	1.21	42424	5.5	24.9	106.8	2.9	128
18	0.172	320	26.5	94.5	4666	0.58	0.44	11.3	41.3	1148	21221	36.9	9433	7.41	2.33	27907	10.6	15.8	92.2	13.5	398
19	0.135	650	40.4	153.3	5556	1.30	0.74	22.0	47.6	2630	22593	56.5	11167	11.11	3.15	34444	18.7	69.6	107.8	17.6	667
20	0.174	391	26.4	52.9	4943	0.57	0.43	9.3	31.8	1523	18534	48.3	9756	5.46	1.87	23707	10.5	24.4	91.1	6.2	1332
21	0.185	480	25.9	77.8	4135	1.76	0.54	8.8	42.4	1635	9892	41.9	6919	6.62	1.89	19459	18.0	20.7	73.4	9.3	791
22	0.154	385	35.2	62.2	5958	0.49	0.49	12.3	32.0	1581	24513	107.5	11607	8.93	2.44	42532	13.5	27.9	103.6	7.3	800
23	0.101	1064	33.7	67.8	7673	0.50	0.74	20.0	87.4	2411	5619	83.9	7970	16.58	2.23	21980	17.6	65.6	96.8	9.7	691
50	0.096	492	24.0	196.1	6016	0.52	-	16.9	43.8	2216	2786	57.0	6354	11.20	1.82	20990	9.9	22.1	226.8	11.5	194
51	0.119	1042	23.3	185.3	4601	0.42	1.47	66.8	52.3	1874	2227	84.2	4181	20.80	4.83	9874	27.9	21.8	87.6	19.3	218
52	0.09	1294	27.8	120.6	6722	0.56	0.83	33.6	86.7	3000	3556	56.9	8083	18.61	3.06	21444	17.8	34.7	113.1	15.6	508
53	0.089	871	24.2	221.6	3567	0.56	0.84	41.3	54.2	2374	3399	34.0	7051	11.80	2.81	21124	15.7	22.5	69.9	23.3	421
54	0.099	1028	31.1	56.1	5253	0.76	0.51	11.9	34.1	1558	3409	35.9	8283	8.84	2.53	31818	16.7	10.9	80.3	8.3	525
55	0.118	1244	30.9	58.7	5297	0.85	-	12.1	93.6	1979	12097	118.6	7542	13.35	2.33	31780	15.9	6.1	125.4	5.9	95
56	0.087	833	24.7	88.5	4770	0.57	-	8.9	28.7	1351	2052	71.3	5920	7.18	1.72	16580	14.1	9.5	71.8	11.2	420
58	0.102	1316	21.8	78.7	4730	0.25	-	9.8	24.0	1887	3725	75.5	5515	8.33	1.96	18113	4.2	6.4	95.8	8.6	71

Table B.3: Dry weight and metal concentrations of the plankton samples of cruise Vulcano0316 in mg/Kg dry weight.

St	m_{dry} (g)	Al	B	Ba	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Mo	Na	Ni	Pb	Sr	V	Zn
1	1.166	63.3	26.2	16.0	9927	2.64	0.32	6.95	8.51	283	16552	-	11985	3.97	2.38	12221	3.58	0.71	-	4.59	69.7
50	0.897	42.4	16.8	15.2	7469	0.75	0.20	1.95	6.44	251	8640	-	6717	3.54	1.25	15190	3.07	0.39	-	2.62	41.8
51	1.111	58.5	23.0	8.4	7561	1.60	0.34	4.03	12.92	893	12489	-	9608	8.75	1.44	21737	3.29	1.37	-	6.50	223.0
52	1.076	45.1	15.5	14.8	6111	0.98	0.19	1.84	9.29	414	8341	-	6854	5.07	1.09	13662	4.14	0.44	-	3.51	30.2
53	1.536	26.7	12.5	-	5387	0.70	0.13	2.25	8.01	115	6999	-	4915	2.56	1.30	9473	2.39	0.37	-	8.06	32.9
54	1.541	12.4	11.3	6.4	5110	0.92	0.11	0.73	5.16	59	7333	-	4543	1.57	0.96	9117	1.69	0.29	-	2.11	13.4
55	0.912	34.8	12.9	16.0	7840	0.90	0.16	1.04	8.39	128	6634	-	5592	3.04	1.21	18421	3.02	0.49	-	2.82	20.8
56	1.077	40.9	22.1	14.0	7916	1.72	0.16	1.53	9.56	171	11978	-	10167	3.78	1.49	21518	3.39	0.77	-	2.27	36.7
57	1.107	19.3	12.8	16.3	4923	1.60	0.14	0.84	6.78	76	8153	-	6346	2.19	1.13	18631	2.64	0.47	-	2.10	22.8
58	1.113	48.3	14.6	16.2	6806	1.75	0.13	1.01	10.85	129	9119	-	6244	3.08	0.97	12668	2.58	0.65	-	2.25	26.1
59	1.290	32.0	18.4	10.7	8372	2.00	0.16	1.03	7.79	109	10097	-	8217	2.54	1.20	10872	2.81	0.45	-	2.36	26.0
61	0.900	23.5	13.4	18.3	6472	1.08	0.17	0.94	7.50	86	8472	-	5861	3.06	1.53	21000	3.42	0.47	-	2.67	18.8
65	1.959	29.2	16.5	7.7	5003	1.21	0.10	0.40	6.02	81	9074	-	7491	1.80	0.45	5819	1.42	0.37	-	1.51	12.8